

## SYMPOSIUM D

# Nonlithographic and Lithographic Methods for Nanofabrication—From Ultralarge-Scale Integration to Photonics to Molecular Electronics

November 26 – December 1, 2000

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\* Invited paper

## TUTORIAL

### FT D: NANOFABRICATION FOR MOLECULAR ELECTRONIC SYSTEMS Sunday, November 26, 2000 2:00 p.m. - 5:00 p.m. Room 201 (Hynes)

Molecular electronics is often regarded as the next revolution in electronics which will be of benefit not only to integrated devices but more generally to information technology. Formidable challenges are still ahead and wiring at the molecular scale is only one example. This tutorial will focus on the critical issues for molecular electronics. A definition of molecular electronics will be provided, along with comparisons to DNA computing and quantum computing. Nanofabrication techniques including potential use of nanolithography will be highlighted.

#### Instructors:

**James M. Tour**, Rice University  
**Lhadi Merhari**, CERAMEC, France

### SESSION D1: NANOSTRUCTURES THROUGH SELF-ASSEMBLY OF COLLOIDAL PARTICLES

Chair: David J. Norris  
Monday Morning, November 27, 2000  
Constitution B (Sheraton)

#### 8:30 AM D1.1

**GUIDED SELF-ASSEMBLY OF LINKED MONOLAYER AND BILAYER ARRAYS OF Au NANOPARTICLES ON SOLID SURFACES.** Jia Liu, Venugopal Santhanam, Rajan Agarwal, Yan Du, Ronald P. Andres, School of Chemical Engineering, Purdue University, West Lafayette, IN.

Close-packed planar arrays of metal nanoparticles that are covalently lined to each other by conjugated organic molecules exhibit interesting lateral electrical conductance. Applications of these linked cluster arrays or "molecular ribbons" have been limited due to the difficulty of selectively depositing them on a solid substrate. We have developed a suite of techniques by which large area ( $> 1 \text{ cm}^2$ ), well-ordered monolayer films of Au nanoparticles can be self-assembled on a water surface and selected portions of these films can be transferred to a solid substrate and linked by various conjugated organic molecules. Double transfers allow us to deposit ordered bilayer arrays.

#### 8:45 AM D1.2

**SIMULATIONS OF EVAPORATION-DRIVEN SELF-ASSEMBLY.** Stephen Rankin, Sandia National Labs, Catalytic & Porous Materials Dept, Albuquerque, NM; Anthony Malanoski, University of New Mexico, Dept of Chemical & Nuclear Engineering, Albuquerque, NM; Frank van Swol, Sandia National Labs and University of New Mexico, Albuquerque, NM.

We examine some of the unique features of evaporation-driven self-assembly using lattice-based Monte Carlo simulations of a ternary mixture of two solvents plus amphiphiles. The simulations are part of a general package being developed which integrates Monte Carlo techniques, density functional theory, and continuum (analytical or numerical) fluid flow modeling (through boundary conditions). Our simulations allow not only conventional bulk simulations of surfactant mesophases (including lamellae, hexagonal close packed cylinders, perforated lamellae, and the bicontinuous "gyroid" phase), but also allow us to approximate interfacial and nonequilibrium phenomena. The amphiphile chains are modeled with a fluctuating bond model, with chain kink, reptation and biased regrowth moves allowed with arbitrary frequencies. Both fixed boundaries (walls) and free boundaries (the vapor-liquid interface) may exist, which allows us to examine mesophase formation in thin film, fiber, and aerosol particle geometries. The vapor-liquid interface can form when all interaction energies are attractive. A novel feature of the simulations is the imposition of composition and chemical potential gradients by defining three contacting control volumes. Two are open and are held at differing chemical potentials. The third is only open to the other two volumes and hence can support a gradient. Both interfaces and concentration gradients orient mesophases (such as lamellar sheets) parallel to themselves. When the interface is of finite dimension (as in a liquid droplet), this alignment can lead to thermodynamically stable onion-like structures similar to observed silicate aerogel particles. As drying drives the transition from one mesophase to another (e.g., from lamellae to hexagonal close packed cylinders), epitaxial relationships can lead to retention of the alignment of an earlier phase (e.g., cylinders parallel to the substrate). Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin

Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

#### 9:00 AM D1.3

**DIRECTED ASSEMBLY AND REAL SPACE ANALYSIS OF (NON-) EQUILIBRIUM COLLOIDAL STRUCTURES.** Jacob P. Hoogenboom<sup>a,b</sup>, Dirk L.J. Vossen<sup>a,b</sup>, Anja K. van Langen-Suurling<sup>c</sup>, Hans Romijn<sup>c</sup>, Alfons van Blaaderen<sup>a,b</sup>. <sup>a</sup>FOM-Institute for Atomic and Molecular Physics, Amsterdam, THE NETHERLANDS; <sup>b</sup>Condensed Matter, Debye Institute, Utrecht Univ, THE NETHERLANDS; <sup>c</sup>Delft Institute of Microelectronics and Submicron Technology, Technical Univ of Delft, THE NETHERLANDS.

Colloidal Epitaxy provides a means to grow large, well-oriented 3D-crystals with characteristic spacings in the photonic range. Under the influence of gravity colloids settle on a patterned wall, which serves as a template for crystallization. These templates were made using various (soft-)lithographic techniques as well as optical tweezer assisted surface tailoring. We show that the control over colloidal structure formation with these methods can be extended from directed self-assembly up to local scale manipulation that is best described as do-it-yourself assembly. Furthermore, with fluorescence confocal microscopy we studied the dynamics of epitaxial crystallization and the role of defects, lattice mismatches and size effects. We present results on epitaxial growth of the first hard sphere hexagonal close packed structure, which has a higher free energy than both the face centered cubic crystal and randomly stacked crystals. Using selectively charged surfaces as templates it is possible to manipulate and study the formation of more open crystals of charged particles. Apart from bulk epitaxial crystallization in suspension, we also used templates and optical tweezers to manipulate the growth of thin colloidal structures in controlled-drying and layer-by-layer processes.

#### 9:15 AM D1.4

Abstract Withdrawn.

#### 9:30 AM D1.5

**TWO DIMENSIONAL CRYSTALLISATION ON CURVED SURFACES.** M. Nikolaidis, M. Hsu, A.D. Dinsmore, A.R. Bausch and D.A. Weitz, Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA.

Self assembly of particles at interfaces is a promising technique for the production of new materials. However, the basic physical interactions governing the self assembly and the appearance of crystalline structures remain elusive. Here we investigated the self assembly of colloidal particles at spherical oil-water interfaces using fluorescence microscopy and particle tracking. Surprisingly, the particles form a two-dimensional crystal that completely covers the curved interface. In order to understand the involved forces, the motion of the particles around their equilibrium positions were analyzed. Further on we examined the dependence of the lattice constant on the geometrical parameters such as curvature and particle size. In addition, we studied the formation of defects in the colloidal-particle lattice. We will discuss the application of our results to new approaches to build materials with novel mechanical properties.

#### 9:45 AM D1.6

**FABRICATION OF PATTERNED SPHERES FOR CONTROLLABLE SELF-ASSEMBLY OF MICRO- AND MESO-STRUCTURES.** Zhenan Bao, Linda Chen, Marcus Weldon, Edwin Chandross, John Rogers, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Self-assembled three-dimensional structures are potentially useful as diffractive optical devices, micromechanical systems, and sensory elements. Such structures have previously been realized by two-photon absorption technique to selectively polymerize desired areas and multilayer photolithography. An alternative method is using colloidal particles as templates in conjunction with sol-gel techniques through the self-assembly of nano- and micro-spheres relying on gravity or pressure to form closely packed periodic structures. It is a time-consuming process and there is little control over the lattice structure of the self-assembly (e.g. simple cubic or diamond). In this talk, we report methods to selectively functionalize defined areas on spheres. This concept would potentially allow us to generate self-assembled structures with controlled parameters, such as periodicity and composition of the structures. Others have reported 3-D mesostructures self-assembled from millimeter-scale objects individually functionalized at selective areas. But our approach can produce relatively large amount of building blocks for further exploring 3-D self-assembled structures.

#### 10:30 AM \*D1.7

**PHOTONIC CRYSTAL CHEMICAL SENSING MATERIALS.** Sanford A. Asher, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA.

Environmentally responsive photonic crystals can be prepared by polymerizing a hydrogel around a crystalline colloidal array (CCA) to form a polymerized colloidal array (PCCA). The PCCA diffracts light due to the periodic lattice formed by the embedded CCA. These photonic crystals can be made responsive to their chemical environment by attachment of molecular recognition agents to the PCCA to form an IPCCA. In the presence of the species recognized by the molecular recognition agent, the IPCCA reponds by changing volume. This shifts the diffraction since the CCA lattice spacing is altered. We have fabricated a number of IPCCA which can detect a series of analytes from metal cations, to glucose etc. We will discuss the basic phenomenology associated with the diffraction and the response of the hydrogel. We will discuss basic sensing motifs associated with charge immobilization, changes in hydrogel crosslinking and changes in the free energy of mixing of the hydrogel.

#### 11:00 AM \*D1.8

PREPARATION AND PROPERTIES MAGNETIC NANOCRYSTAL SUPERLATTICES: SELF-ASSEMBLING MAGNETIC RECORDING MEDIA. Shouheng Sun, C.B. Murray, IBM Corp T.J. Watson Research Center, Yorktown Heights, NY.

We discuss the synthesis of monodisperse magnetic nanocrystals and their assembly into well order nanocrystal superlattices. Examples for low to moderate coercivity(Ku) materials like nickel and cobalt will be presented along high coercivity systems of interest for future recording applications. In particular iron-platinum (FePt) nanoparticles will be used as a model high (Ku) material. Preparation of monodisperse magnetic nanocrystals by reduction metal salt precursors and decomposition of metal carbonyls will be emphasized. Both the cobalt and FePt particle systems can be produced with sizes tunable from 3 to 10 nm diameter with a standard deviation less than 5%. These nanoparticles self-assemble into two dimensional (2D) and three dimensional (3D) superlattices. Thermal annealing is found to convert the internal particle structure of the cobalt from the cubic to hexagonal forms while the FePt transforms from a chemically disordered face centered cubic phase to chemically ordered face centered tetragonal phase. These thermal treatments produce chemically and mechanically robust magnetic thin films with. The FePt can support high-density magnetization reversal transitions (recording).

#### 11:30 AM D1.9

HIGH DENSITY FERROMAGNETIC NANOWIRE ARRAYS OBTAINED FROM ORDERED POROUS ALUMINA TEMPLATES. Kornelius Nielsch, Ralf Wehrspohn, Jochen Barthel, Jürgen Kirschner, Frank Müller, Ulrich Gösele, Max-Planck-Institut für Mikrostrukturphysik, Halle, GERMANY; Saskia F. Fischer und Helmut Kronmüller, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY.

We have shown recently that ordered porous alumina arrays can be obtained with a sharply defined pore diameter by a two-step electrochemical anodization process of aluminum. The interpore distance ( $D_{INT}=50\text{...}500\text{ nm}$ ), the pore diameter ( $0.25\bullet D_{INT} \leq D_P < D_{INT}$ ) and length (100 nm... 200  $\mu\text{m}$ ) can be varied over a large range [1]. Here, we are demonstrating the application of highly ordered porous alumina for perpendicular high density magnetic media. Areal density of about 300 Gbit/in<sup>2</sup> can be achieved with this approach. Nickel and Cobalt nanowires were grown in highly ordered pores of anodic alumina membranes using pulsed electrodeposition. A complete metal filling of the pore arrays with a pitch of 100 nm was obtained [2]. The bulk magnetic behavior of our nanostructures were analyzed by SQUID measurements. The Cobalt sample showed a preferential magnetic orientation perpendicular to the wires due to a strong magnetic anisotropy. In contrast, the nickel sample has its magnetic orientation along the axis of the wires. Coercive fields of more than 1000 Oe and squareness of the hysteresis loop of  $\approx 80\%$  were detected. Moreover, we will discuss the influence of the nanowire diameter on the magnetization. MFM investigations validated the single domain magnetic behavior of the Ni nanowires. [1] A.-P. Li, F. Müller, A. Birner, K. Nielsch, and U. Gösele, J. Appl. Phys. 84, 6023 (1998). [2] K. Nielsch, F. Müller, A.P. Li and U. Gösele, Adv. Mat. 12, 582 (2000).

#### 11:45 AM D1.10

ARRAYS OF MAGNETIC PARTICLES AT THE LIQUID-AIR INTERFACE. Tianhao Ji, Y. Saado, M. Golosovsky, and D. Davidov, Racah Institute of Physics, The Hebrew University of Jerusalem, ISRAEL.

We have recently shown self-assembly of macroscopic magnetic particles on the liquid surface into tunable ordered crystalline structure and the potential of these systems for photonic bandgap applications. In this study we demonstrate that the lattice constant and the perfectness of the crystalline lattice depend on the number of

particles in a predictable way. We measure propagation of electromagnetic waves through a stack of 4-6 layers and show evidence for a photonic stopband. We report fabrication of magnetic microparticles with similar properties. We use poly(styrene-co-divinylbenzene) microspheres and by chemical means encapsulate into them magnetic nanoparticles. We achieve high values of magnetization of 20 emu/g. We also overcoat these spheres with a thin layer of gold. Since gold has a pronounced plasmon resonance, optical properties of such microparticles strongly depend on the thickness of the gold layer. These particles will be used as building blocks for PBG applications in the infrared. Optical properties will be tuned by varying the thickness of the gold layer, while self-assembly and variable lattice constant will be achieved through magnetic forces between the particles and external magnetic field.

#### SESSION D2: TEMPLATE-DIRECTED SYNTHESIS OF NANOSTRUCTURES

Chair: David J. Norris  
Monday Afternoon, November 27, 2000  
Constitution B (Sheraton)

#### 1:30 PM \*D2.1

DISPERSING DENDRIMERS IN POLYMER MATRICES AND THEIR USE AS TEMPLATES FOR NANOPARTICLE SYNTHESIS. Barry J. Bauer, Franziska Gröhn, Brent D. Viers, and Eric J. Amis, National Institute of Standards and Technology, Gaithersburg, MD.

Polyamidoamine (PAMAM) and polypropyleneimine (PPI) dendrimers can be dispersed in polymeric matrices on a molecular level as shown by small angle neutron scattering (SANS) and by small angle x-ray scattering (SAXS). By dissolving the dendrimers in a polymerizable alcohol such as 2-hydroxyethyl methacrylate and forming the polymer in situ, the dendrimers remain in the matrix as separate molecules. Similarly, the terminal groups of the dendrimers can be reacted with end functionalized polyethylene glycol (PEG) forming well dispersed dendrimers. Dendrimers in the matrix can be used as templates for the formation of nanoparticles in a way previously demonstrated for dendrimers in solution. A variety of materials can be dispersed this way that retain the dispersion of the dendrimers themselves.

#### 2:00 PM D2.2

SOLVATOCHROMIC BEHAVIOR OF THREE-Dimensionally ORDERED MACROPOROUS (3DOM) MATERIALS FROM COLLOIDAL CRYSTAL TEMPLATES. Christopher F. Blanford, Rick C. Schroden, Andreas Stein, Univ of Minnesota, Dept of Chemistry, Minneapolis, MN.

Samples of three-dimensionally ordered macroporous ("3DOM") metal oxides have been synthesized from latex colloidal crystal templates and solutions metal alkoxides. The highly porous products exhibit a striking opalescence in visible light. The color of these materials shifts to a higher wavelength when the pores are impregnated with a liquid. The shift in wavelength (as observed by diffuse reflectance UV-vis spectroscopy) was about 350 nm per refractive index unit. This linear relationship between wavelength and refractive index was used to extrapolate the filling fraction of the dielectric material in the structure and the spacing between the pores. The predicted pore spacing was comparable to the pore spacing measured by scanning electron microscopy (SEM). The color change may be exploited as a refractive index sensor for flow applications.

#### 2:15 PM D2.3

DOUBLE-TEMPLATING AS A ROUTE TO NEW PHOTONIC BAND GAP STRUCTURES. Peng Jiang, Rice Univ, Dept of Chemistry, Houston, TX; Rajesh Rengarajan, Rice Univ, Dept of Electrical and Computer Engineering, Houston, TX; Mary E. Turner, Rice Univ, Dept of Chemistry, Houston, TX; Daniel Mittleman, Rice Univ, Dept of Electrical and Computer Engineering, Houston, TX; Vicki L. Colvin, Rice University, Dept of Chemistry, Houston, TX.

Existing strategies for preparing monodisperse colloids and colloidal crystals, generally manipulate the chemistry of colloidal formation. Only silica and some polymer colloids, however, can be routinely prepared with the narrow size distributions required for forming high quality colloidal crystals. Here we report a physical rather than chemical strategy for forming colloids with size distributions under 5%, and their corresponding colloidal crystals. Our "double-template" approach is so termed because we form our colloids by templating inside the cavities of a macroporous polymer which itself is a template of a silica colloidal crystal. Freed from the constraints of solution chemistry, we are able to generate a wide variety of highly monodisperse inorganic (CdS, AgCl, TiO<sub>2</sub>, ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) and polymeric (polyurethane and polypyrrole)solid colloids, core-shell colloids (ceramic/metal, ceramic/ceramic, ceramic/polymer), as well as hollow colloids with controllable shell thickness. Moreover, our

method results in the direct formation of a colloidal crystal and does not require control over the sedimentation process, a difficult issue for denser inorganic colloids. Thus, we can form colloidal crystals of virtually any colloid. For the case of hollow sphere colloidal crystals we find evidence for strong photonic behavior. The transmission spectra exhibit an optical stop band, whose spectral position and width depend on the thickness of the shell and the overlap between adjacent spheres, in a manner consistent with numerical simulations. These parameters can be controlled over a wide range, thus permitting systematic studies of the optical properties, and providing a valuable new method for engineering the characteristics of the optical stop band in colloidal photonic media. A new method of making monodisperse colloids and colloidal crystals with a wide size range (40 nm to 500 nm), which can be simply tuned by temperatures, from a special polymer template will also be discussed.

#### 2:30 PM \*D2.4

NOVEL MATERIALS AND DEVICES VIA TEMPLATED ASSEMBLY OF COLLOIDAL PARTICLES. Orlin D. Velev, Peter M. Tessier, Abraham M. Lenhoff, Eric W. Kaler, Dept of Chemical Engineering, Univ of Delaware, Newark, DE.

This talk will present three complementary examples of formation of materials and devices by templated, colloiddally engineered, assembly of particles. An example of what we call "inside-out" templating is the formation of nanostructured materials by replicating of the long-ranged ordered structure of colloidal crystals into a solid matrix. These structured macroporous materials can find use as catalysts, membranes and as photonic crystals. One type of templated porous structure of specific practical interest is thin supported films of porous metals. We show that such films can serve as high-quality SERS substrates, which are created at only a fraction of the cost of their microfabricated analogues. Our second strategy of "outside-in" templating is to control the overall outer shape of the assemblies and create self-sustained objects or functional patches. The "templates" in the first example of this strategy are electrically addressable patterns on a glass surface. Microscopic electronically readable IgG sensors are assembled in situ from the latex particles used in agglutination assays by combining dielectrophoresis with tuning of the colloidal forces. The limit of detection of the miniature biosensors is comparable to that of the commercial assays and can potentially be increased much further. As a second example of "outside-in" templating, we present a new class of microstructured particles synthesized by crystallizing latex microspheres inside aqueous droplets suspended on the surface of fluorinated oil. This method yields highly ordered and symmetric 3D supraparticles of millimeter dimensions with interesting optical properties and good structural stability. The particle shape can be adjusted controllably from spherical, through ellipsoidal and discoidal, to toroidal "doughnuts". Anisotropic composites, such as spheres that are only half-magnetic and that can be flipped by magnetic fields, have been obtained.

#### 3:30 PM \*D2.5

PANOSCOPIC SILICON - A MATERIAL FOR "ALL" LENGTH SCALES. Emmanuel Chomski and Geoffrey A. Ozin, Materials Chemistry Research Group, Chemistry Department, University of Toronto, Ontario, CANADA.

Silicon is the "veteran" semiconductor in the management of electrons. The recent quest for opto-electronic and photonic materials suggests that new architectures of silicon structured over multiple length scales may still be the optimum material for the transition from electron based to photon based computers and communication systems. The focus of this lecture is to briefly look at recent research accomplishments in fabrication and self-assembly methods of shaping elemental silicon over nanometer to micrometer length scales for applications in electronics, optoelectronics and photonics. This work will appear in print as a Research News Article in *Advanced Materials* July 2000

#### 4:00 PM D2.6

COLLOIDAL CRYSTALLIZATION WITHIN MICROCHANNEL NETWORKS FOR PHOTONIC CRYSTAL PATTERNING. Abbas Rizvi, Benjamin Messer, Peidong Yang, Department of Chemistry, University of California, Berkeley, CA.

Uniform colloidal spheres are self-assembled into close packed lattice within microchannel networks. These close-packed lattices are then used as template for fabricating patterned macroporous (SiO<sub>2</sub>, TiO<sub>2</sub>, Si, Ge) materials. The self-organization process is monitored in real time with video optical microscope. Single domain photonic crystals made of macroporous silica or titania can be readily patterned on substrate. The microstructures (orientations and interface) can be rationally modified by choosing different microchannel dimensions and colloidal sphere sizes. This process represents an effective and inexpensive approach for the fabrication of photonic crystal circuits for microscopic light manipulation purpose.

#### 4:15 PM D2.7

Abstract Withdrawn.

#### 4:30 PM \*D2.8

POLYMERIC NANOSTRUCTURES INDUCED BY SUBSTRATE CORRUGATION. N. Rehse, M. Geoghegan, C. Wang, R. Magerle, Georg Krausch, Universitaet Bayreuth, LS Physikalische Chemie II, Bayreuth, GERMANY.

We discuss the influence of small substrate corrugations on the wetting behavior of thin homopolymer films. As model substrates we use miscut silicon wafers, which form a shallow surface grating on suitable UHV annealing. Below a characteristic thickness, homopolymer films tend to dewet such substrates and form regular arrays of linear channels of nanoscopic width. We show that the characteristic thickness is related to the radius of gyration of the molecules indicating an entropy driven instability of the films.

### SESSION D3: NANOSTRUCTURES THROUGH SELF-ASSEMBLY OF BLOCK-COPOLYMERS

Chair: Younan Xia

Tuesday Morning, November 28, 2000

Constitution B (Sheraton)

#### 8:30 AM \*D3.1

STRUCTURED POLYMERIC LIQUID FILMS: PATTERN FORMATION AND PHASE BEHAVIOR. Peter F. Green<sup>1,2,3</sup>, Ratchana Limary<sup>2</sup>. <sup>1</sup>Department of Chemical Engineering, <sup>2</sup>Graduate Program in Materials Science, and <sup>3</sup>Texas Materials Institute. The University of Texas at Austin and the Texas Materials Institute, Austin, TX.

During the last decade, research on thin, sub-micron, block copolymer films was devoted toward understanding and controlling microstructural formation of thin films in the temperature regime  $T < T(\text{ODT})$ , where thermodynamic interactions favored the formation of ordered microstructures.  $T(\text{ODT})$  is the order-disorder transition temperature. We show that in the temperature range where thermodynamic interactions favor a completely homogeneous state,  $T > T(\text{ODT})$ , thin copolymer films exhibit features that are akin to the behavior of simple homopolymer fluids, yet at the same time, maintain some features that are inherently associated with block copolymers. Films in this regime  $T > T(\text{ODT})$  experience a substrate induced ordering. When the film thickness,  $h$ , is thinner than a critical thickness,  $h_{crit}$ , the film dewets via the nucleation and growth of discrete holes or by a "spinodal-like" process, depending on the actual value of  $h$ . When  $h = h_{crit}$ , the film is stable, whereas when  $h > h_{crit}$  a so-called "autophobic" dewetting process occurs, leaving a layer height  $h_{crit}$ .  $h_{crit}$  is related to the interlamellar spacing,  $L$ , of the copolymer in the ordered state. Eventually, the system evolves into large droplets on the layer.

#### 9:00 AM D3.2

SELECTIVE ELECTROLESS METAL DEPOSITION WITHIN BLOCK COPOLYMER MICRODOMAINS. Yot Boontongkong, Robert E. Cohen, Michael F. Rubner, MIT, Cambridge, MA.

We have demonstrated a method for the directed formation of layered metallic copper structure within the subsurface morphology of a bulk lamellar block copolymer. Using an electroless deposition process, copper was selectively deposited inside the interconnected microdomain network of the water-permeable block containing pre-loaded palladium ions. The method relies on the diffusion of electroless plating reagents through the lamellar network; the same microdomain network also serves as template for the selective copper deposition. The extent of the deposition can be controlled by adjusting the deposition rate and deposition time. The relatively simple process yields a novel nanoscale composite consisting of alternating layers of metallic copper with those of the insulating hydrocarbon matrix. We are currently investigating the electrical properties of the nanocomposite; we expect that such an alternating layered structure would display electrical anisotropy with respect to the lamellar orientation. In addition, we are employing similar technique to selectively deposit other metals - e.g., cobalt and nickel - within block copolymer microdomain templates.

#### 9:15 AM D3.3

FABRICATION OF NANOPATTERNED THIN FILMS USING SELF ASSEMBLED BLOCK COPOLYMER LITHOGRAPHY. J.Y. Cheng, C.A. Ross, V.Z.H. Chan, E.L. Thomas, M.I.T. Dept. Materials Science and Engineering, Cambridge, MA; R.G.H. Lammertink, G.J. Vancso, Univ. Twente, Dept. Materials Science and Technology of Polymers, NETHERLANDS.

Block copolymers provide a method for patterning nanoscale arrays of

dots on a thin film over large areas. In this work, we have used poly(ferrocenyldimethylsilane-*b*-isoprene) (PFS-*b*-PI) and poly(ferrocenyldimethylsilane-*b*-isoprene) (PFS-*b*-PS) as the template to fabricate metal dots over area of a few square centimeters. The polymer thin film is spun onto a substrate to form a self-assembled array of spheres or cylinders of, for example, PFS in a PS or PI matrix. This pattern is then transferred into underlying layers using a combination of etching processes to define an array of nanoscale metal dots. The morphologies and stability of the block copolymer thin films are optimized through annealing and adjusting surface tension and composition to produce stable, hexagonally packed sphere or perpendicular cylinders. We have also found that the long range order of the pattern is improved by the presence of shallow grooves in the substrate. The PI and PS are removed anisotropically by oxygen reactive ion etching (RIE) while PFS is converted into an etch-resistant iron-silicon-oxide. CF<sub>4</sub>/O<sub>2</sub>-RIE was found to be an effective method to further transfer the pattern into an underlying tungsten layer with dots size of order 10nm and period of 30nm. The RIE conditions are adjusted to give hexagonally packed tungsten dots with good height contrast, furthermore, these tungsten dots can serve as a hard mask for patterning films of other materials using ion milling. We will present results for block copolymers chosen to produce arrays of dots and will show how these patterns are transferred into magnetic films such as cobalt to produce array of magnetic dots for high density magnetic data storage.

#### 9:30 AM \*D3.4

HIGH-THROUGHPUT CHARACTERIZATION OF PATTERN DIRECTED POLYMER DEWETTING. Amit Sehgal, and Alamgir Karim, Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD.

The dewetting of thin polymer films in the presence of a symmetry breaking surface energy field results in spontaneous self-organization to generate surface relief structures. The mechanism of the dewetting processes are sensitive to film thickness, and the spatial resolution and symmetry of the underlying chemical pattern. In this study, the topography and morphology of dewetting thin homopolymer (polystyrene, PS) films on chemically patterned self-assembled monolayers (SAM) are investigated by AFM and optical microscopy. Thickness range from the regime of ultra-thin film spinodal dewetting (~10 nm) to relatively larger dimensions (~100nm). A discrete variation of the periodic chemical pattern width (1-15 microns) across the surface enabled simultaneous measurement on a range of pattern dimensions. Automated methods were employed for patterning over extensive areas facilitating the creation of film thickness gradients. Such a "high-throughput" approach allows for rapidly screening the dewetting behavior of polymers for the entire range of pattern widths and film thickness, from non-confining to confining behavior. The control of such spontaneous random phenomena may be used to create surface topologies that can serve as polymeric platforms for nanoscale templated applications.

#### 10:30 AM \*D3.5

SELF-ASSEMBLY OF HARD PARTICLES IN DIBLOCK-COPOLYMERS MELTS: FORMATION OF ORDERED ORGANIC/INORGANIC STRUCTURES. Anna C. Balazs, June Huh, Valeriy Ginzburg, Univ of Pittsburgh, Dept of Chemical and Petroleum Engineering, Pittsburgh, PA.

We investigate the influence of hard nanoparticles on the phase behavior of diblock copolymers. Using Monte Carlo simulations, we obtain phase diagrams as a function of the nanoparticle size and concentration. When the size of the nanoparticles becomes comparable to the radius of gyration of the minority (A) block, we observe the formation of new superstructures, where the particles self-assemble inside the copolymer micelles. We develop a theoretical model, based on the strong segregation limit approximation, and show that such structures can indeed be equilibrium (most likely metastable) phases. The formation of such phases is due to the interplay between the particle-particle excluded-volume interactions, preferential particle/block-A interactions, and the enthalpic and stretching interactions within the diblock.

#### 11:00 AM \*D3.6

CONTROLLING THE ORDERING OF DIBLOCK COPOLYMER THIN FILMS USING CHEMICALLY NANOPATTERNED SUBSTRATES. Paul Nealey, Xiao M. Yang, Richard D. Peters, Department of Chemical Engineering and Center for NanoTechnology, University of Wisconsin, Madison, WI.

Block copolymers have tremendous potential for applications in nanofabrication because these systems self-assemble into periodic structures (spheres, cylinders, or lamellae) with domains with length scales of 10 nm to 100 nm. We are investigating the use of thin films of block copolymers as templates for patterning at the sub 50 nm scale. Many advanced applications of these templates in nano-

technology may be feasible if addressable arrays could be created. Our research focuses on controlling the self-assembly process in thin films of block copolymers so as to: 1) induce perpendicular orientation of domains to the substrate, 2) achieve perfection in ordering over macroscopic dimensions in the plane of the film, and 3) register the periodic structure in the polymer film with features of the underlying substrate. To realize these objectives, we have developed a process that combines advanced lithography and novel imaging layers based on self-assembled monolayers to create chemically patterned surfaces that guide the ordering of thin films of block copolymers based on wetting behavior.

#### 11:30 AM D3.7

NANOPATTERNING OF THE SURFACES FOR MOLECULAR BIOLOGY APPLICATIONS. Y.S. Seo, V. Samuilov, J. Sokolov, M. Rafailovich, Dept of Materials Science, SUNY at Stony Brook, NY; S. Delagrangue, Polyteck, Nants, FRANCE; R. Di Nardo, Brookhaven National Laboratory, NY; A. Ulman, Polytechnic University, NY.

We use a diblock-copolymer system, self-assembled using L-B technique, to produce patterns at the nanometer length scale, which is not easily accessible by conventional lithography techniques. The micellar size (~100 nm) and intermicellar distance (~300 nm) can be controlled by changing concentration of spreading solution and molecular weight of copolymer, which directly related to aggregation number of micelles. This structure was used as a template for introducing metal nanopatterns on semiconductor surfaces by reactive ion beam etching. Monolayers of UTS were used for modification of gold patterned and initial surfaces. The thickness of patterned gold layer was comparable with the persistence length of DNA molecules. The experimental study of the influence of chemical patterning on the electrical transport of long DNA molecules on the surfaces is presented. This work was supported by NSF-MRSEC Program.

#### 11:45 AM D3.8

TOPOGRAPHICAL CONTROL OF ORDER IN ASYMMETRIC DIBLOCK COPOLYMERS. Rachel A. Segalman, Hideaki Yokoyama, Edward J. Kramer, University of California, Santa Barbara, Depts. of Chemical Engineering and Material Science, Santa Barbara, CA.

Highly asymmetric diblock copolymers in thin films phase separate to form spheres on the order of tens of nanometers. We demonstrate that the ordering of these spheres may be controlled by utilizing the preferential attraction of one block to the surfaces of polymer thin film. In the case of asymmetric poly(styrene-*b*-vinylpyridine) (PS-PVP) diblock copolymers in thick films, this surface attraction can induce layering of spherical microdomains resulting in long range order perpendicular to the surface. In the plane of the substrate, the spheres are arranged into hexagonal arrays that are randomly oriented. Well defined lateral surface structures can also be induced in much thinner films consisting of a single layer of spheres. This done by controlling the interaction between the confining surfaces of the film and the blocks of the copolymer. For instance, the imposition of a topological pattern on the film surface results in a perfectly packed hexagonal array of spheres in 2-D. A confined stripe of copolymer is ordered in a single crystalline, close packed structure with hexagonal symmetry for stripe widths as wide as 4  $\mu$ m, with a definite epitaxial orientation relationship between the edges of the stripe and the close packed directions in the layer. We then use this technique to observe grain defect evolution and surface effects on the crystalline order in this diblock copolymer sphere system. Such control may prove useful in lithographic applications of block copolymer films.

### SESSION D4: UNCONVENTIONAL APPROACHES TO NANOFABRICATION

Chair: Younan Xia  
Tuesday Afternoon, November 28, 2000  
Constitution B (Sheraton)

#### 1:30 PM D4.1

Abstract Withdrawn.

#### 1:45 PM D4.2

A SOFT LITHOGRAPHIC APPROACH TO THE FABRICATION OF 1D, 2D AND 3D NANOSTRUCTURES OF SINGLE CRYSTALLINE SILICON. Yadong Yin, Byron Gates, Younan Xia.

We have recently demonstrated an effective approach based on soft lithography to the large-scale fabrication of 1D, 2D, and 3D nanostructures of single crystalline silicon. Typical examples include nanowires, nanorods (with ultrasharp ends), rings, and wood-pile stacks of silicon nanowires. In this talk, we will present the experimental procedure, as well as the unique applications of these nanostructure in high-resolution imaging and fabrication of photonic bandgap crystals.

**2:00 PM \*D4.3**

UNCONVENTIONAL METHODS OF FABRICATION OF NANOSTRUCTURES. George M. Whitesides, Heiko Jacobs, Chris Love, Kateri Paul, Daniel Wolfe, Ming-Hsien Wu, and Cheng Zu, Harvard University, Dept of Chemistry, Cambridge, MA.

"Nanotechnology" is still largely a misnomer: there are few established technologies that require classically fabricated nanostructures. Nanoscience is, however, unarguably a very attractive area for exploration and development. Nanostructures have largely been fabricated by techniques developed in the microelectronics world: e-beam writing, advanced photolithographic methods, scanning probe systems. These methods have many strengths, but the weakness that they require techniques and equipment that are often not familiar/available outside electronics and materials science. Chemical synthesis has also begun to play an important role (buckytubes and -balls; quantum dots). Given the uncertainty in the applications for which nanostructures will ultimately be used, it would be useful to have available relatively simple fabrication procedures that could be used to generate them easily using a range of materials: these procedures would make it possible for a range of communities—including biologists, chemists, and others who often do not have access to the sophisticated systems being developed to fabricate nanostructures for electronic applications—to experiment with nanostructures, and would accelerate the identification of targets for their application. This talk will summarize a range of low-cost methods for fabricating nanostructures. These methods will center around applications of soft lithographic methods: both in printing/molding, and in photolithography.

**2:30 PM \*D4.4**

NANOIMPRINT LITHOGRAPHY (NIL) AND LITHOGRAPHICALLY-INDUCED SELF-ASSEMBLY (LISA) FOR FUTURE VLSI. Stephen Y. Chou, Wei Zhang, Wei Wu, Hua Tan, Lei Chen, Paru Deshpande, Larry Zhuang, and Longting He, NanoStructure Laboratory, Department of Electrical Engineering, Princeton University, Princeton, NJ.

We present recent developments of two new nanopatterning paradigms, that have a great potential to impact the future of VLSI and material growth. The first new paradigm is nanoimprint lithography (NIL), that patterns a resist by physical deformation of the resist shape with embossing, rather than by modification of the resist chemical structures with radiation as in conventional lithographies [1]. NIL has demonstrated sub-10 nm feature size, 40 nm period, and good uniformity over a large area. A number of methods for NIL, such as planar, roller, and step-and-repeat press, as well as multi-level alignments and device fabrication by NIL will be presented. The second new nanopatterning paradigm is the recent discovery of lithographically-induced self-assembly (LISA), where a mask is used to induce and control self-formation of periodic supramolecular polymer pillars [2]. An initial flat polymer thin film self-forms a pillar array by raising against the gravitational force and surface tension. The pillar array has a single domain lattice and well-controlled position for each pillar. In principle, the LISA process should be extended to other material systems. The video of the dynamic formation and a theory of LISA, as well as the applications of LISA in interconnects and photonic-band-gap materials will be presented. [1]S.Y. Chou, P.R. Krauss, and P.J. Renstrom, *Appl. Phys. Lett.*, 67(21), 3114 (1995) and *Science*, 272, 85 (1996) [2] S.Y. Chou and L. Zhuang, (a) unpublished 1997, and (b) S.Y. Chou, L. Zhuang, *J Vac Sci Tech B* 17 (6), 3197-3202, 1999

**3:30 PM \*D4.5**

PARALLEL DIP-PEN NANOLITHOGRAPHY: A NEW TOOL FOR GENERATING AND STUDYING SOFT NANOSTRUCTURES. Chad Mirkin, Northwestern University, Dept of Chemistry, Evanston, IL.

A new type of ultrahigh resolution parallel soft-lithography, Dip-Pen Nanolithography (DPN), that is interfaceable with biomolecules and biofunctionalized building blocks will be presented. This soft lithography allows one to routinely pattern structures, in serial or parallel fashion, with sub 50 nm spatial and line-width resolution with near-perfect alignment. Implications in materials synthesis, electronics, and bionanotechnology will be discussed.

**4:00 PM D4.6**

ELECTROCHEMICAL SYNTHESIS OF MULTI-MATERIAL NANOWIRES AS BUILDING BLOCKS FOR FUNCTIONAL NANOSTRUCTURES. David J. Peña<sup>a</sup>, Baharak Razavi<sup>b</sup>, Peter A. Smith<sup>b</sup>, Jeremiah Mbindyo<sup>a</sup>, Sheila R. Nicewarner<sup>a</sup>, Benjamin Martin<sup>a</sup>, Brian D. Reiss<sup>a</sup>, Michael J. Natan<sup>a</sup>, Theresa S. Mayer<sup>b</sup>, Thomas E. Mallouk<sup>a</sup>, and Christine D. Keating<sup>a</sup>. <sup>a</sup>Department of Chemistry, The Pennsylvania State University, University Park, PA; <sup>b</sup>Department of Electrical Engineering, The Pennsylvania State University, University Park, PA.

Nanostructures are electrochemically deposited into alumina or polycarbonate templates resulting in monodisperse, anisotropic particles with a range of tunable sizes. These particles have been synthesized with diameters of 20-250 nm and with lengths of 1-10  $\mu\text{m}$ . Currently, structures have been made with stripes of Au, Ag, CdSe, Co, Cu, Ni, Pd, and Pt. These materials offer a variety of different properties. In particular, many of the metals in this group are excellent conductors, meaning these particles can actually be used as nanowires. Co and Ni are ferromagnetic and may be used for separation or assembly. CdSe is a semiconductor, possibly allowing for the synthesis of electronic devices such as transistors. Furthermore, many of these materials have different surface chemistries, making the orthogonal functionalization and assembly of these nanowires more accessible. This research focuses on increasing the number of materials available, especially semiconductors, incorporating these potentially useful materials into multilayered nanowires and evaluating their electrical properties, either individually or in small bundles. In addition, the surface chemistry of the various materials in the nanowires is being compared to aid in orthogonal self-assembly of functional nanostructures such as memory devices. The work presented will demonstrate the effects of rod composition on electrical properties. In particular, the effects of changing the work function of the materials on either side of a semiconductor to form Schottky junctions or Ohmic contacts will be presented. Also, the effects of using semiconductors with different band gaps and sizes will be shown.

**4:15 PM D4.7**

NANOFABRICATION USING SELF-ASSEMBLED ALUMINA TEMPLATES. Oded Rabin<sup>a</sup>, Paul R. Herz<sup>b</sup>, Yu-Ming Lin<sup>b</sup>, Akintunde I. Akinwande<sup>b</sup>, Mildred S. Dresselhaus<sup>b,c</sup>, Massachusetts Institute of Technology, <sup>a</sup>Dept of Chemistry, <sup>b</sup>Dept of Electrical Engineering and Computer Science, <sup>c</sup>Dept of Physics, Cambridge, MA.

Porous anodic alumina films consist of a self-assembled array of parallel channels with controllable diameters. These films are becoming a versatile tool for nanofabrication and nonlithographic patterning in the 10-250 nm range. This study presents new architectures fabricated by a combination of traditional lithography and the use of alumina templates. Porous alumina films are grown on silicon wafers from deposited aluminum layers. Patterned layers above and below the aluminum layer are used for the area-selective growth and etching of the porous film. The application of this technique for the fabrication of nanowire/alumina composites, dense arrays of field emitters and 2D photonic crystal devices, is demonstrated.

**4:30 PM D4.8**

NANOSPHERE LITHOGRAPHY: SELF-ASSEMBLED PHOTONIC AND MAGNETIC MATERIALS. Christy L. Haynes, Amanda J. Haes, Richard P. Van Duyne, Northwestern University, Dept of Chemistry, Evanston, IL.

Early work with size-tunable periodic particle arrays (PPAs) fabricated by nanosphere lithography (NSL) demonstrated that the localized surface plasmon resonance (LSPR) could be tuned throughout the visible region of the spectrum. Further developments of the NSL technique have produced a myriad of nanoparticle configurations. Presented in this paper are several array types and examples of their utility in current applications. Both the sensitivity and tunability of the LSPR have been firmly established using single layer PPAs. Magnetic force microscopy (MFM) has been used to show that double layer PPAs act as single domain magnets and give strong MFM contrast. Angle-resolved NSL has produced nanogap and nano-overlap structures with manipulation resolution of one nanometer. Nanowell structures extend the original two-dimensional structure into the third dimension. Exploitation of this flexible, materials-general NSL technique allows for investigation of the catalytic, electrochemical, magnetic, optical and thermodynamic properties of nanoparticles.

**4:45 PM D4.9**

TOPOGRAPHY-FREE, FUNCTIONALIZED NANOSTRUCTURES CREATED BY ULTRAFLAT NANOSPHERE LITHOGRAPHY. Wolfgang Frey, Ashutosh Chilkoti, Duke University, Dept. of Biomedical Engineering, Durham, NC.

We have designed a new method, ultraflat nanosphere lithography (UNSL), to easily fabricate periodic features on the submicron scale, which are needed for many applications ranging from surface-enhanced spectroscopy to quantum structures and nanostructured biofunctional surfaces. UNSL creates periodic nanopatterned surfaces of well-defined size and minimal topography for different materials that are also stably bonded. The nanofeatures as well as the matrix that the features are embedded in are capable of orthogonal self-assembly chemistry. Additionally, for the study of cell surface-interactions, UNSL creates a nanopatterned surface of minimal height variation in

order to decouple physico-chemical and topographical effects on cell behavior. UNSL is based on nanosphere lithography and ultraflat template stripping. Material  $M_1$  is evaporated onto mica through a mask formed by self-assembled hexagonally packed nanospheres. After the spheres have been lifted off the substrate, evaporation of material  $M_2$  embeds the nanopattern in a much thicker matrix. A substrate is glued to the surface for mechanical support. Finally, the mica is stripped off, revealing an ultraflat pattern of nanotriangles of  $M_1$  embedded in  $M_2$ . In order to demonstrate the feasibility of UNSL, we have chosen pairs of materials  $M_1$  (Au, Ag) and  $M_2$  (Al, SiO) so that  $M_1$  and  $M_2$  can be independently functionalized by orthogonal self-assembly chemistry, and transparent samples and insulator-conductor pairs can also be created. We have visualized the nanopatterns fabricated by UNSL using AFM, SEM and imaging Auger electron spectroscopy, and have demonstrated that the surface roughness is below 1 nm (rms) over large areas.

#### SESSION D5: ADVANCED LITHOGRAPHIC TECHNIQUES

Chairs: Lhadi Merhari and Kenneth E. Gonsalves  
Wednesday Morning, November 29, 2000  
Constitution B (Sheraton)

##### 8:30 AM \*D5.1

**EXTREME ULTRAVIOLET LITHOGRAPHY FOR THE ULTIMATE IN SILICON SCALING.** S. Vaidya, D. Sweeney, Lawrence Livermore National Laboratory; R. Stulen, Sandia National Laboratory; D. Attwood, Lawrence Berkeley National Laboratory, Livermore, CA.

Extreme Ultraviolet Lithography holds the promise of high-throughput at minimum resolution, and as such, could well represent the "ultimate" lithography employed for manufacturing integrated circuits down to the limits defined by silicon device physics. LLNL, SNL, and LBL have been participating in an industry-supported research program in pursuit of this goal. This talk will summarize our progress to date.

The Engineering Test Stand full-field scanning exposure system will be printing sub-100nm images as early as 2001; and design and construction of a small-field micro-exposure tool with ~35nm resolution is well underway. Optics fabrication and coating capabilities have evolved to deliver diffraction limited imaging capability, and a handshake with potential vendor-partners for technology transfer has been initiated. Deposition systems have been optimized for minimizing mask defect densities, and coating schemes evolved for planarizing substrate defects. Systems with laser-produced plasma sources promise cost-competitiveness with alternate lithographic approaches and recent experiments with much less expensive discharge sources are encouraging. Commercial deep-ultraviolet resist materials are demonstrating resolution and edge-roughness commensurate with requirements for sub-100nm design rules, while pattern transfer studies with bilayer imaging schemes have demonstrated image fidelity down to 50nm. These results will be illustrated and remaining hurdles to technology commercialization discussed.

Work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48. Funding was provided by the Extreme Ultraviolet Limited Liability Corporation under a cooperative research and development and supported by International Sematech.

##### 9:00 AM \*D5.2

**MATERIALS CHALLENGES AND ALTERNATIVES FOR ADVANCED PHOTOLITHOGRAPHIC PATTERNING: FROM 193 TO 157 NM AND BEYOND.** Elsa Reichmanis, Omkaram Nalamasu, Francis M. Houlihan, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

In the last decade, major advances in fabricating electronic devices have placed increasing demands on microlithography, the technology used to generate today's integrated circuits. Within the next few years, a new form of lithography will be required that routinely produces features of less than 0.1 micron. As the exposing wavelength of light decreases to facilitate higher resolution imaging, the opacity of traditional materials precludes their use; and major research efforts to develop alternate materials are underway. Through understanding of materials structure and its relationship to device process requirements and performance, cyclo-olefin based polymers provide for sub-0.1 micron imaging capability using 193 nm exposure. Alicyclic monomers such as norbornene are readily copolymerized with other units to afford a wide range of alternative matrices that exhibit transparency at the exposing wavelength and aqueous base solubility. Further reduction in imaging wavelength necessitates renewed research to define alternative materials platforms. Materials

transparency is the key issue to be addressed for 157nm or EUV lithography. Novel polymer architectures including fluorinated polymers will be required to effect sufficient transparency coupled with requisite solubility, sensitivity, contrast, etching resistance, shelf-life and purity. Each of these issues will be discussed from the perspective of polymer materials chemistry.

##### 9:30 AM D5.3

**CHROMIUM OXYCARBONITRIDE PHASE SHIFTING PHOTOMASKS IN TERMS OF CHEMISTRY AND STRUCTURE.** Jack Smith, D.A. Bonnell, University of Pennsylvania, Dept of Materials Science and Engineering, Philadelphia, PA; Roger H. French, DuPont Co., Central Research, Wilmington, DE.

The latest deep ultra-violet (DUV) photomask technology requires that macroscopic properties such as optical transmission, reflectance, and chemical reactivity be precisely controlled. Therefore, a fundamental understanding of the relationship between atomic bonding and nm scale property variation is required. Thin films of Cr-O-C-N are compositionally graded to produce specific attenuation and phase shift of optical radiation. A combination of techniques is used to relate the local atomic bonding to macroscopic properties. Sputtered neutral mass spectroscopy is used to resolve local composition, and variable angle spectroscopic ellipsometry is used to determine local optical properties (on nm scale) that are then related to local composition. Core level shifts in X-ray photoemission spectroscopy characterize changes in the Cr environment associated with changes in composition. A model is suggested in which bonding at the atomic level is controlled within different 10-100 nm sized regions which are then combined to produce arbitrary optical properties.

##### 9:45 AM D5.4

**NONLITHOGRAPHIC AND LITHOGRAPHIC METHODS FOR NANOFABRICATION.** D. Arayasantiparb and M. Libera, Stevens Institute of Technology, Hoboken, NJ.

Among the factors controlling the spatial resolution associated with electron-beam lithography is the excitation of fast secondary electrons (FSE's) by scattering between incident high energy electrons and atomic electrons in a polymeric resist. The FSE's can travel in directions roughly perpendicular to the incident beam direction and can have energies on the order of several keV or more. This effect has been modeled for several decades using Monte Carlo methods, but no good methods have been developed to study it experimentally. This research uses 200 keV electrons in a field-emission scanning transmission electron microscope (STEM) to both induce and measure delocalized polymer-damage effects outside the region of primary electron irradiation. Measurements are made on thin (100 nm) unsupported films of poly(styrene) and aromatic epoxy. A characteristic pi-pi star transition at approximately 7 eV energy loss associated with aromatic rings is used to monitor radiation-induced changes in the polymer. Spatially-resolved energy-loss measurements using a focused electron probe approximately 3 nm (FWHM) in diameter show that aromatic character is affected as much as 60 nm away from the point of incident irradiation. The data can be collected and presented in a manner which describes a degradation profile as a function of distance from the point of primary incidence. The degradation profiles scale with the primary radiative dose. Measurements are made both at room temperature and at 175 K. No difference is observed between these.

##### 10:30 AM \*D5.5

**STATUS OF ION PROJECTION LITHOGRAPHY.** Wilhelm H. Bruenger, Fraunhofer Institute for Silicon Technology, Itzehoe, GERMANY.

Under the umbrella of a MEDEA project a consortium headed by Infineon Technologies runs a worldwide development program to establish ion projection as new generation lithography technique. While a process development tool is under construction at IMS, Vienna, the experimental ion projector at Fraunhofer, Berlin, is used to investigate critical issues of this technology. Areas of concern are resist process and open stencil mask stability. 50 nm resist structures with high aspect ratios suffer from pattern collapse, T-topping, and limited solubility of exposed resist in narrow channels. These problems have been addressed by changing drying procedures, using negative instead of positive resist, and by choosing resist matrixes with higher solubility. Open stencil masks have to be protected against swelling by ion implantation. Different types of protective layers have been tested including stress compensated carbon and conductive polyimide. The multi cusp ion source operated with He is now run with hydrogen to benefit from the more uniform energy deposition per resist depth. Direct surface modification without a resist is a promising application for ion technology. Ongoing work on structuring of magnetic films and the modification of diamond like carbon layers will be reported.

**11:00 AM D5.6**

FABRICATING TWO-DIMENSIONAL METAL-NANOCRYSTAL ARRAYS USING PULSED-LASER DEPOSITION AND FOCUSED-ION-BEAM TECHNOLOGIES. R.F. Haglund, Jr., Leonard C. Feldman, Cynthia E. Heiner, Matthew D. McMahon, Robert H. Magruder, III, Allen T. Newton, Ricardo Ruiz, Liyong Shen and Robert A. Weller, Vanderbilt University, Department of Physics and Astronomy, Department of Electrical Engineering and Computer Science and Department of Mechanical Engineering, Nashville, TN.

The combination of resonant optical response and rapid relaxation times has generated substantial interest in fabricating optical devices such as closely-coupled metal nanocrystals for processing optical signals through near-field or dipole-dipole coupling. The fabrication of such devices, requires extraordinary control of growth processes at nanometer length scales. It is particularly difficult to combine materials of widely differing surface energies at this size scale, yet it is precisely these materials which are most intriguing for optical devices because of the mismatch in electronic properties. We are using physical, rather than chemical, synthesis and processing in order to produce nanostructures in which metal nanocrystals are embedded in laterally ordered arrays in dielectric thin films. Our approach is based on the use of focused ion-beam (FIB) and pulsed-laser deposition (PLD) technologies both singly and together. For example, we have used the FIB to pattern substrates for subsequent growth of metal nanoclusters by PLD. So far we have fabricated: one-dimensional photonic bandgap materials, based on PLD-deposited multilayers of silver and alumina, exhibiting multiple bandpasses and high electrical conductivity; linear and planar arrays of metal nanoclusters using the FIB alone; and nanoclusters grown by PLD on dielectric films previously textured with regularly spaced defect sites created by the FIB. Analysis of growth kinetics, composition, structure and optical properties by a variety of microscopic and spectroscopic probes, including atomic-force and electron microscopy, ion backscattering and four-point electrical probes, will be presented, as well as discussions of potentially interesting applications. This work was supported in part by the National Science Foundation under the Major Research Instrumentation program. CEH and MDM were supported by a Research Experience for Undergraduates Program of the Division of Materials Research, National Science Foundation.

**11:15 AM D5.7**

DEMONSTRATION OF ARRAYS OF SUB-MICROMETER SOLID-STATE FRESNEL LENSES FOR ELECTRONS. Yasuo Ito, Andrew L. Bleloch, University of Cambridge, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

The advent of high-brightness field emission guns for scanning transmission electron microscopy has made it possible to use finely focused electron beams to directly drill holes a few nanometer in size and of controlled depth in some inorganic thin films. Such patterned structures can then be used to manipulate the phase of an electron wave in a manner analogous to light optics. Here we demonstrate the focusing action of a compact solid state pixelated Fresnel phase (PFP) lens for electrons (700 nm in diameter), consisting of an array of holes ("pixelated") in an AlF<sub>3</sub> thin film deposited on carbon thin film. The depth of the holes, hence the phase of the exit electron wave is varied as a function of radius from the center of the pattern so that the wavelet from each hole can be in phase on axis at a designated focal point thus producing a lens. Two types of lenses, convergent and divergent, with nominal focal length of 1 mm for 200 keV electrons were produced. The estimated full-width-half-maximum of the focus is 8 nm. With improvement of the efficiency, these lenses may find applications in electron-beam lithography, in X-ray optics and in light optics. For example, with a combination of micro-machined structures, an array of the PFP lenses could be used for parallel patterning of prescribed parts of field emission transistors. There seems to be little difficulty with present computer-controlled equipment to make one thousand lenses on a single thin substrate. Also, the fabrication technology of the PFP lenses can be applied to fabrication of photonic crystals.

**11:30 AM D5.8**

PLANAR HIGH TEMPERATURE SUPERCONDUCTING JOSEPHSON JUNCTIONS FABRICATED BY COMBINATION OF FOCUSED ION BEAM NANOFABRICATION AND ION IMPLANTATION. Hong-Ying Zhai, Quark Chen, Jia-Rui Liu, Wei-Kan Chu, Univ of Houston, Dept of Physics and Texas Center for Superconductivity, Houston, TX.

Planar high temperature superconductor-normal layer-superconductor (SNS) Josephson junctions have been fabricated using combination method of Focused Ion Beam (FIB) nanofabrication and medium energy Co ion implantation. These junctions are made on Y-Ba-Cu-O thin films grown on LaAlO<sub>3</sub>. Measured current - voltage curves show SNS junction behaviors. The devices are totally YBCO based both superconductor and normal layer, the normal layer region has been

shrunk to 50-100 nm. With improved procedure, All YBCO based SIS junction can be expected using this combined technique.

**11:45 AM D5.9**

FABRICATION OF TEMPLATES ON FLAT AND CURVED SURFACES USING ELECTRON BEAM LITHOGRAPHY AND REACTIVE ION ETCHING. Kee W. Rhee and Loretta M. Shirey, Nanoelectronics Processing Facility, Electronics Science and Technology Division, Naval Research Laboratory, Washington, DC.

Templates for contact printing applications have been fabricated on both flat and curved surfaces using electron beam lithography. Flat templates were fabricated on silicon substrates by simple chrome lift-off process and reactive ion etching (RIE). For fabrication of curved templates, however, both convex and concave quartz lenses of 25.4 mm diameter with a 103.0 mm radius of curvature were utilized. A chrome layer of 50 nm thickness was sufficient to suppress charging from the thick lens before spin-coating the curved surfaces with a layer of poly(methylmethacrylate) (PMMA). However, in order to compensate the curvature of the lens, special beam focusing scheme was employed for lithography. The detailed description of this is included. Lithography was done using an electron beam nanowriter at 50 kV and 30 pA. A collection of patterns including starbursts, gratings, and pads of various sizes were repeatedly written covering wide areas of the lens surface. E-beam patterned PMMA was developed, followed by pattern transfer into the chrome underlayer by wet etch. Final pattern transfer into the quartz lens was done using the plasma reactive ion etching. Features down to 200 nm have been patterned and transferred into the quartz substrate to a depth of ~600 nm, with an etch depth variation of less than 10% across the sample. This approach provides a convenient method of fabricating flat and curved templates for contact printing application with readily available techniques; electron beam lithography and reactive ion etching.

SESSION D6: NOVEL MATERIALS FOR NANOLITHOGRAPHY

Chairs: Lhadi Merhari and Marie-Isabelle Baraton  
Wednesday Afternoon, November 29, 2000  
Constitution B (Sheraton)

**1:30 PM D6.1**

Abstract Withdrawn.

**1:45 PM D6.2**

DEVELOPMENT OF INDUCED CRYSTALLIZATION AS PATTERN TRANSFER MECHANISM FOR NONLITHOGRAPHIC NANOFABRICATION. M.J. Cabral<sup>1</sup>, T. Chraska<sup>2</sup>, S. Mesarovic<sup>2</sup>, D.M. Longo<sup>2</sup>, E.A. Stach<sup>3</sup>, J.C. Bean<sup>1</sup>, and R. Hull<sup>2</sup>. <sup>1</sup>Department of Electrical Engineering, University of Virginia, Charlottesville, VA; <sup>2</sup>Department of Materials Science and Engineering, University of Virginia, Charlottesville, VA; <sup>3</sup>National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA.

A novel nanoscale printing technology based upon direct contact between nanofabricated printheads and amorphous films/substrates is being developed. Transfer of features from printhead to substrate is via an induced crystallization mechanism, with a goal of controlling crystal nucleation at dimensions comparable to the printhead features. To realize such a printing mechanism, appropriate mediums/materials that can be crystallized through physical and/or thermal contact with the printhead elements have to be identified. From a broad range of suitable amorphous materials we focus on Ge, SiGe, and ITO films grown by molecular beam epitaxy or sputtering. The crystallization may be induced directly by heating (thermally), pressure (mechanically), or electrical conduction through the contact points. Crystallization of many amorphous materials is known to be self sustaining (so called explosive crystallization). A number of different samples have been tested by a special heating printhead fabricated with a Focused Ion Beam (FIB). A series of such experiments allow us to establish an optimum thickness of amorphous films at which the induced crystallization is laterally confined to the smallest possible dimensions corresponding to the original feature size on the printhead. A mathematical model suggests the feasibility of achieving lateral confinement of the induced crystallization. In order to characterize fully the transitional and final substrate states, a real-time observation of nanoscale crystallization mechanism will be carried out in the transmission electron microscope (TEM). A special TEM goniometer is being developed which incorporates a piezoelectrically driven tip and a heating capability to enable observation of tip-substrate contact at elevated temperatures that should give invaluable insight into crystallization mechanisms.

**2:00 PM \*D6.3**

MATERIALS FOR e-BEAM NANOLITHOGRAPHY.  
Elizabeth A. Dobisz, Naval Research Laboratory, Washington, DC.

The work focuses on materials issues in e-beam nanolithography. It begins with an examination of polymeric resists in e-beam lithography. The talk describes e-beam patterning of a variety of substrates, from conductors, insulators, to curved surfaces. Next applications of self assembled monolayers for e-beam lithography is outlined. SAMs have been found useful as both imaging layers and in forming discharge layers. The issues in utilizing high voltage, low voltage and proximal probe lithographies will be discussed.

#### 2:30 PM \*D6.4

**FULLERENE NANOCOMPOSITE RESIST FOR NANO-LITHOGRAPHY.** Tetsuyoshi Ishii, Atsushi Yokoo, NTT, Basic Research Laboratories, Kanagawa, JAPAN; Toshiaki Tamamura, NTT Electronics Corp., Kanagawa, JAPAN; Kiyotaka Shigehara, Tokyo Univ of Agriculture and Technology, Tokyo, JAPAN.

As ultra-thin film resist is increasingly required for the realization of nanometer dimensions, the resistant quality of resist materials has become a critical issue in nanolithography. Carbon reinforcement by fullerene incorporation into conventional resist film improves dry-etching resistance and the improved resistance thereby increases resolution since the resist film can be made extremely thin. A fullerene (C60/C70 mixture) nanocomposite of a positive-type electron beam resist, ZEP520, shows a substantial increase in resistance to reactive ion etching and enables us to fabricate a 15-nm gate pattern by using a film thinner than that needed for ordinary ZEP resist. The sensitivity of the fullerene nanocomposite of ZEP readily changes with fullerene content due to the dissolution inhibiting effect of fullerene, and this unique characteristic can be employed to construct a fullerene-incorporated bilayer resist system for lift-off. A system comprising a fullerene-incorporated ZEP top layer and a pure ZEP bottom layer presents an ideal overhang pattern and facilitates mold fabrication for nanoprinting. Presently, extensive application of the fullerene nanocomposite of ZEP and also composites made from systems other than ZEP are limited due to the poor solubility of fullerene. However, the solubility of fullerene can be enhanced by introducing some solubility-promotion moiety to a fullerene molecule. We have synthesized several fullerene derivatives and observed considerable solubility enhancement in both the ZEP resist solvent and other common solvents. The solubility enhancement makes it possible for us to incorporate a fullerene derivative into ZEP up to 50 wt% with a minimal decrease of sensitivity. Further, combining a fullerene-derivative with chemical amplification resist promises to increase sensitivity of nanocomposite resist. Such an advanced fullerene nanocomposite resist system is briefly examined.

#### 3:30 PM \*D6.5

**HIGH-RESOLUTION RESISTS FOR NEXT GENERATION LITHOGRAPHIES: THE NANOCOMPOSITE APPROACH.** Kenneth E. Gonsalves, Yongqi Hu, Hengpeng Wu, Polymer Program at the Institute of Materials Science and Department of Chemistry, University of Connecticut, Storrs, CT; Lhadi Merhari, CERAMEC R&D, Limoges, FRANCE.

The SIA roadmap predicts mass production of sub-100nm resolution circuits by 2006. This not only imposes major constraints on next generation lithographic machines but also requires that new resists capable of accommodating such a high resolution be synthesized. Except for ion beam lithography, DUV, X-Ray, and electron beam lithographies suffer significantly from proximity effects, leading to severe degradation of resolution in classical resists. We report on a new class of resists based on organic/inorganic nanocomposites having a structure strongly reducing the proximity effects. Synthetic routes will be described for a ZEP520/nano-SiO<sub>2</sub> resist where 47nm wide lines have been written with a 40nm diameter 20kV electron beam at no sensitivity cost. Other resist systems based on polyhedral oligosilsesquioxane methacrylate polymerised with MMA, TBMA, MAA and a proprietary PAG will be presented. These nanocomposite resists suitable for DUV and electron beam lithographies show enhancement in both contrast and RIE resistance in oxygen. Tentative mechanisms responsible for proximity effect reduction will be discussed. This work has been partly supported by DARPA and NSF.

#### 4:00 PM \*D6.6

**SELF-ASSEMBLED MONOLAYERS AS HIGH RESOLUTION ETCH MASKS AND TEMPLATES FOR ORGANIC MOLECULAR ASSEMBLY.** C. Harnett, A. Lopez, S. Kayyar, and H.G. Craighead, Applied and Engineering Physics, Cornell University, Ithaca, NY.

We have used a variety of self-assembled monolayers as resists for low energy electron beam patterning. These compounds can be used as high-resolution patternable linker molecules for selected area binding of proteins and other organic compounds. As these systems can be positioned in registry to existing patterns this allows the positioning of organic systems with the accuracy of electron beam lithography. We have also explored the use of self-assembled monolayers for the

replication of lithographically defined systems for the creation sub-wavelength artificial dielectric systems. The ultra-thin layers can be used with contrast-enhancing etching processes to etch high aspect ratio structures. This can be used to create diffractive optical devices in a single step process.

#### 4:30 PM D6.7

**ON-WAFER SPECTROFLUOROMETRIC EVALUATION OF 193 NM PHOTOACID GENERATORS.** Gilbert D. Feke, Robert D. Grober, Yale Univ, Dept of Applied Physics, New Haven, CT; Gerd Pohlers, Kathryn Moore, James F. Cameron, Shipley Co, Marlborough, MA.

Chemically amplified resists (CARs) that employ acid catalysts are widely used throughout the semiconductor industry due to the need for high throughput in the lithography process. The acid pattern is generated by the photolytic decomposition of a photoacid generator (PAG) in response to the lithographic radiation. The acid is then activated by a postexposure bake to catalyze reactions in the resist and thereby create the differential dissolution rate. The photospeed of CARs therefore depends directly on the acid generation efficiency of the PAG during exposure. Evaluation of the efficiency of PAGs is an important component of resist design. We report the evaluation of candidate PAGs for 193 nm CARs using an on-wafer spectrofluorometric technique. This technique, first reported by Feke et al. [J. Vac. Sci. Technol. B 18, 136 (2000)] for X-ray CARs, involves doping the resist formulations containing the candidate PAGs with pH-sensitive fluorescent molecules, coating one wafer per PAG, patterning the wafers with a dose ramp, and spectroscopically imaging the wafers. Coumarin 6, a dye that was introduced as an acid sensor by Pohlers et al. [Chem. Mater. 9, 3222 (1997)] is used as an improved pH-sensitive fluorophore for this application. The efficiency curve of each PAG is spatially encoded in the fluorescence image of each wafer. This technique is convenient, fast, robust, and non-destructive. We discuss the optimization of this technique to the evaluation of prototype 193 nm PAGs.

#### 4:45 PM D6.8

**PATTERNABLE FLUOROCARBON AND ORGANOSILICON CVD THIN FILMS.** Hilton G. Pryce Lewis, Massachusetts Institute of Technology, Dept of Chemical Engineering, Cambridge, MA; Gina L. Weibel, Christopher K. Ober, Cornell University, Dept of Materials Science and Engineering, Ithaca, NY; Karen K. Gleason, Massachusetts Institute of Technology, Dept of Chemical Engineering, Cambridge, MA.

Thin films produced by chemical vapor deposition (CVD) show promise as materials capable of undergoing patterning by lithographic means. In this paper, we consider the use of fluorocarbon and organosilicon films deposited by hot filament CVD (HFCVD) for producing nanometer-scale features. HFCVD is a non-plasma technique which offers the ability to tailor the chemistry of films with polymer-like structure. Both fluorine- and silicon- containing polymeric materials are under consideration as candidates in next-generation microelectronics technologies. Their transparency makes them ideal resist candidates for 157-nm lithography, and their low dielectric constant makes them strong contenders as interconnect materials. As one part of this paper, we present a collaboration aimed at merging the role of resist and low-k dielectric. Specifically, we are investigating a direct dielectric patterning process in which a material is deposited by CVD, exposed, and developed using no wet chemistry. The film is exposed using e-beam or a 157-nm source, and developed using supercritical CO<sub>2</sub> as a dry developing medium. The patterned film then serves as a low-k interconnect material. This technology would greatly simplify future device manufacture by reducing the number of steps involved in patterning. Furthermore, supercritical CO<sub>2</sub> offers many processing advantages over wet development, including improved resolution and the prevention of pattern collapse. With such a scheme, we have demonstrated positive-tone contrast in fluorocarbon HFCVD films and fully-developed images of 500-nm have been obtained from e-beam exposure. In another aspect of this work, the novel structure of organosilicon HFCVD films makes them potentially exciting materials for nanofabrication. Thin films deposited from cyclic precursors are extremely smooth and show evidence of incorporation of ring structures. Ring size may thus determine resolution limits for patterning such a material.

SESSION D7/JJ9: JOINT SESSION  
MOLECULAR DEVICES  
Chair: Alamgir Karim  
Thursday Morning, November 30, 2000  
Constitution B (Sheraton)

#### 8:30 AM D7.1/JJ9.1

**FABRICATION AND CHARACTERIZATION OF METAL-**

MOLECULE-METAL TUNNEL JUNCTIONS BY CONDUCTING PROBE ATOMIC FORCE MICROSCOPY. C. Daniel Frisbie, David J. Wold, Dept of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN.

Molecular level electrical transport studies require innovative approaches for making electrical contacts to oriented molecules. Conducting probe atomic force microscopy (CP-AFM) provides a convenient approach to electrically contacting monolayer films and the formation of metal-molecule-metal junctions. In CP-AFM, a metal-coated AFM tip is placed in direct contact, under controlled load, with the material to be probed. The technique differs from STM in that the probe is positioned using normal force feedback, which decouples probe positioning from electrical measurements. Using this technique, we show that CP-AFM may be used to make mechanically stable electrical contact to self-assembled monolayers (SAMs) on Au. We have probed the current-voltage (I-V) characteristics of the resulting junctions as a function of the number of SAM thickness and the load applied to the tip-SAM contact. The ease of this technique and the fine control of the probe during measurements make CP-AFM a promising approach for studying transport through molecular junctions. Further studies of the dependence of the junction resistance on conjugation, functional group distributions, molecular orientations, and dimensions will also be discussed.

**8:45 AM D7.2/JJ9.2**

CARBON NANOTUBE BASED NONVOLATILE RANDOM ACCESS MEMORY FOR MOLECULAR COMPUTING. Thomas Rueckes, Kyoungha Kim, Ernesto Joselevich, Charles M. Lieber, Harvard University, Dept of Chemistry and Chemical Biology, Cambridge, MA.

A new concept for molecular electronics exploiting carbon nanotubes as both molecular device elements and molecular wires for reading and writing information has been developed. Each device element is based on a suspended, crossed nanotube geometry that leads to bistable, electrostatically switchable on/off states. The device elements are naturally addressable in large arrays by the carbon nanotube molecular wires making up the devices. These reversible, bistable device elements could be used to construct nonvolatile random access memory and logic function tables at an integration level of  $10^{12}$  elements/cm<sup>2</sup> and an element operation frequency in excess of 100 GHz. The viability of this new concept is demonstrated both by detailed calculations and by the experimental realization of a reversible, bistable nanotube-based molecular electronics bit.

**9:00 AM \*D7.3/JJ9.3**

DESIGN AND MEASUREMENT OF MOLECULAR ELECTRONIC SWITCHES. M.A. Reed, Departments of Electrical Engineering and Applied Physics, Yale University, New Haven, CT.

Electron transport studies in molecular-scale systems have recently become possible with the utilization of advanced microfabrication and self-assembly techniques. We have performed the measurement of the conductance of a single molecule using a break junction technique [1], the demonstration of molecular diodes [2], and the systematic investigation of metal-molecule contacts in a variety of systems [3]. Most recently, we have observed [4] large and useful reversible switching behavior in an electronic device that utilizes molecules as the active component, specifically a nitroamine redox center. The molecular device exhibits negative differential resistance (NDR) and peak-to-valley ratios exceeding 1000:1 and exceeds that observed in typical solid state quantum well resonant tunneling heterostructures. The designs of molecular switches, memories, and their circuit applications will be discussed.

1. M.A. Reed et al., *Science* 278, 252 (1997).
2. C. Zhou et al., *Appl. Phys. Lett.* 71, 611 (1997).
3. J. Chen et al., *Chem Phys Lett* 313, 741 (1999).
4. J. Chen et al., *Science* 286, 1550 (1999).

**9:30 AM \*D7.4/JJ9.4**

ADVANCES IN MOLECULAR ELECTRONICS: SYNTHESIS AND TESTING OF NANOSCALE MOLECULAR DEVICES. D.W. Price, S.M. Dirk and J.M. Tour, Center for Nanoscale Science and Technology, Rice University, Houston, TX; J. Chen and M.A. Reed, Department of Electrical Engineering, Applied Physics, and Physics, Yale University, New Haven, CT.

With the miniaturization of current silicon-based electronics possibly approaching its hypothesized limit of 0.01 microns, new realms of electronics are being explored. Our team has shown that single organic molecules can carry significant amounts of electronic current, which has led to a great amount of research in this area. Further, we demonstrated devices with negative differential resistance (NDR) having a peak to valley ratio in excess of 1000:1, which is 10 times that of typical solid state devices. These same devices also display retention of electrons enabling the compounds to act as memory

components. The NDR and memory effects were first seen in a solid state "nanopore" device utilizing a self-assembled monolayer comprised of  $\sim 1000$  conjugated organic molecules. The physical and chemical nature of these effects are currently being explored using cyclic voltammetry and theoretical calculations to explain the effects and possibly predict properties of future molecular devices. Advances in compound synthesis and development will be described.

**10:30 AM \*D7.5/JJ9.5**

DRIVEN DYNAMICS OF MOLECULAR DEVICES AND ASSEMBLIES AT THE NANOSCALE. Alison Noble-Luginbuhl, Hye Jin Kwon, Renee Blanchard, Ralph G. Nuzzo, University of Illinois at Urbana-Champaign, Department of Chemistry, Urbana, IL.

The properties of molecular devices—systems with electrooptical or electronic responsiveness, for example—depend very sensitively on the organizational state of their constituents. The dynamics of these systems, especially those underlying driven processes which effect phase changes in the materials, can be extraordinarily complex and vary sensitively with the dimensions of the structures. In this talk I will describe detailed studies of such cooperativities, especially as are seen in examples of molecular devices that are textured at the nanoscale. Of particular interest to us, and a focus of our recent work, are the roles played by surface interactions and near-surface organization in mediating the structural and field-driven dynamical properties of nanometer-scale organic assemblies exhibiting liquid crystalline order. I will describe fabrication methods and chemistries for surface modification that enable the direct study of such phenomena.

**11:00 AM \*D7.6/JJ9.6**

CHEMICALLY ASSEMBLED MOLECULAR ELECTRONICS CIRCUITRY. Jim Heath, Fraser Stoddart, Pat Collier, Yi Luo and Eric Wong, Department of Chemistry and Biochemistry, UCLA, Los Angeles, CA.

Architectures, devices, and small-scale circuitry will be presented for a chemically assembled molecular electronic nanocomputer. Various reconfigurable switches, capable of robust operation under ambient conditions, will be discussed. Various nano-scale wiring networks, using silicon nanowires and single-walled carbon nanotubes, will be presented and the electronic properties of these networks will be discussed. Schemes for coupling molecular switches and nano-scale wiring structures will be discussed.

**11:30 AM D7.7/JJ9.7**

DEFINING  $<10$  NM GAPS USING STEP-EDGE LITHOGRAPHY AND IN-SITU TUNNELING CURRENT MEASUREMENTS. Mark J. Dalberth, John C. Price, Charles T. Rogers, University of Colorado-Boulder, Dept. of Physics, Boulder, CO.

The measurement of current-voltage characteristics of a single molecule is an important milestone on the road to utilization of molecular electronics. The difficulty in this measurement lies not only in the attachment of a single molecule across a gap, but in the fabrication of the molecule-sized gap itself. We report on a technique for the fabrication of  $<10$  nm gaps. Starting with a step ion milled into a silicon dioxide substrate, we use electron beam lithography to define a channel in bi-layer electron beam resist that runs across the step at 90 degrees. The gap for molecular attachment is created by evaporating metal over the step, and, as the metal film thickness increases, the gap closes. During metalization, we monitor tunneling current across the gap giving us an in-situ measure of gap width.

**11:45 AM D7.8/JJ9.8**

CURRENT AMPLIFICATION USING TWO BACK-TO-BACK UNIMOLECULAR RECTIFIERS IN A LANGMUIR-BLODGETT MONOLAYER BETWEEN ALUMINUM ELECTRODES. Tao Xu and Robert M. Metzger, Dept. of Chemistry, University of Alabama, Tuscaloosa, AL.

Some time ago we confirmed that *g*-hexadecylquinolinium tricyanoquinodimethanide C<sub>16</sub>H<sub>33</sub>Q<sub>-3</sub>CN<sub>3</sub>, is a unimolecular rectifier both by nanoscopic and macroscopic means [1,2]. We are interested in verifying gain in a three-electrode molecular device. We transferred a 2.3 nm thick [1] Langmuir-Blodgett (LB) monolayer of C<sub>16</sub>H<sub>33</sub>Q<sub>-3</sub>CN<sub>3</sub> on a base electrode B (100 nm thick Al), then evaporated several cylindrical Al electrodes (1.0 to 1.5  $\mu$ m diameter, 100 nm thick, 1  $\mu$ m apart), atop the cryocooled monolayer. By Ga/In eutectic drops, Au wires were connected to the base electrode B, and to two adjacent Al pads, call them A and C. The two pads were, one forward-biased (voltage VAB), the other back-biased (voltage VBC). Current amplification or transistor action was not expected from this device, because of the formal absence of a "base" or "gate" or "grid" region. We were astonished that a measurable current amplification was found. When VAB=0, the current IBC, as a function of VBC, was

very small for  $VBC < 0$ ;  $IBC = 0$  at  $VBC = 0$ ,  $IBC$  is large and positive for positive  $VBC$ , as before [1]. As  $VAB$  is increased from 0 to 0.8 Volts,  $IBC$  decreases dramatically in the first quadrant, and becomes larger (more negative) in the third quadrant. In the first quadrant current amplification factors of up to 2.5 were seen. In the third quadrant the amplification factors were less than 1. The LB monolayer is an electrical insulator in the plane of the monolayer, so this is not a field-effect transistor. For amplification to be understood, energy transfer within the monolayer, or some role of the Al electrodes (with their defective oxide coverings) may account for what we have found: current amplification in a device involving two molecules.

We thank DOE-EPSCoR (DE-FC02-91-ER-75678) for financial support.

[1] R.M. Metzger, et al., J. Am. Chem. Soc. 119: 10455 (1997).

[2] R.M. Metzger, Acc. Chem. Res. 32: 950-957 (1999).

## SESSION D8: PHOTONIC PROPERTIES OF NANOSTRUCTURES

Chair: Alamgir Karim

Thursday Afternoon, November 30, 2000

Constitution B (Sheraton)

### 1:30 PM \*D8.1

FTIR SPECTROMETRY AS A QUALITY CONTROL METHOD FOR SURFACE ENGINEERING OF NANOMATERIALS.

Marie-Isabelle Baraton, SPCTS-UMR 6638 CNRS, University of Limoges, Limoges, FRANCE.

For a long time, scientists have modified surface properties of materials by adsorbing organic molecules onto their surfaces. Surface modifications are indeed a way to obtain controlled surface properties and often constitute the first step in making self assembled materials. While there is no doubt on the industrial importance of surface modification and surface engineering, how the surface chemical composition is modified and how the surface reactivity is perturbed are fundamental questions not always clearly answered. Moreover, it should be envisaged that if the modified surface has to be in contact with different chemical environments, the surrounding molecules may compete with the grafted chemical groups and therefore an equilibrium will be reached possibly to the detriment of the original surface modifications. For this fundamental study, Fourier transform infrared (FTIR) spectrometry is a relevant tool particularly well suited to the analysis of the surface species on nanosized particles. In this work, surface modifications of nanosized powders will be followed in situ by FTIR spectrometry, making it possible to determine the surface chemical reactions leading to new grafted species. The perturbations of these grafted surface species under humid environment will be highlighted. Consequences of surface modifications on bulk properties, such as electrical conductivity will be discussed.

### 2:00 PM \*D8.2

SYSTEMATIC OPTIMIZATION OF POLYMERIC ELECTRO-OPTIC MATERIALS. Larry R. Dalton, Department of Chemistry, University of Washington, Seattle, WA.

Chromophore-containing polymeric electro-optic materials must satisfy many requirements before they can be considered for use in applications at telecommunication wavelengths (1.3 and 1.55 microns). These include large macroscopic electro-optic activity, low optical loss, and stability (thermal, chemical, and photochemical). Such materials must be capable of being integrated with silica fiber optics and semiconductor electronics. We discuss design of chromophores not only for large hyperpolarizability but also for low optical loss and for thermal and photochemical stability. The processing of these materials to maximize electro-optic activity while minimizing processing-associated optical loss is discussed. Device structures appropriate for minimizing insertion loss are discussed, as is the fabrication of such devices and three-dimensional active/passive optical circuits. The identification of new structure/function relationships provide design criteria for future improvements as well as permitting better definition of the performance limitations that can be expected for polymeric electro-optic materials prepared by electric field poling methods. A number of new device applications will be discussed.

### 2:30 PM \*D8.3

NANOPHOTONICS: NANOSCALE OPTICAL MATERIALS AND INTERACTIONS. Paras N. Prasad, Christopher S. Friend, Yuzhen Shen, Przemyslaw P. Markowicz, Jacek Swiatkiewicz, Jeffrey Winiarz, Abani Biswas, Photonics Research Laboratory, Institute for Lasers, Photonics and Biophotonics, Departments of Chemistry, Physics, Electrical Engineering and Medicine, State University of New York at Buffalo, Buffalo, NY.

Nanophotonics defined as nanoscale optical science and technology is

a new frontier, which includes nanoscale confinement of radiation, nanoscale confinement of matter and nanoscale photophysical or photochemical transformation. Selected examples of our research work in each of these areas are presented here. Nonlinear optical interactions involving nanoscale confinement of radiation is both theoretically and experimentally studied using near-field geometry. The effort in nanoscale confinement of optical domains is focused to control excitation dynamics and energy transfer as well as to produce photon localization using nanostructured rare-earth doped glasses and novel inorganic-organic photorefractive nanocomposites. Spatially localized photochemistry using a near-field two-photon excitation is being developed for nanofabrication and nanoscale memory.

### 3:30 PM \*D8.4

PHOTONIC CRYSTAL LASERS AND COUPLERS FABRICATED BY OPTICAL AND SOFT-LITHOGRAPHY. Ananth Dodabalapur, R.E. Slusher, J. Rogers, A. Timko, M. Meier, O. Nalamasu, D. Tennant, Bell Laboratories, Lucent Technologies, Murray Hill, NJ; A. Mekis, M. Ibanescu, and J. Joannopoulos, MIT, Cambridge, MA.

Optical lithography (at 193 nm or 248 nm) has been successfully employed to define two-dimensional photonic crystals with triangular, square, and honeycomb symmetries. The periodicity achieved was as low as 340 nm for triangular lattices. Photo-excited lasers have been fabricated from such photonic crystals by employing organic semiconductor based gain media. Soft-lithographic methods have also been used to fabricate similar structures. These lasers emit in the visible and are convenient to image. Laser action occurs at points in the 2-D Brillouin zone where the density of photon states is peaked and where the photon group velocity goes to zero. Laser action does not necessarily take place at band extrema, occurring at saddle points where the density of states is sometimes higher. We have also found a variety of ways to combine lasers and couplers resulting in composite devices with interesting and potentially useful optical properties.

### 4:00 PM \*D8.5

SURFACE PLASMON PHOTONICS: HOW TO GET LIGHT THROUGH SUB-WAVELENGTH APERTURES. Thomas W. Ebbesen, Laboratoire des Nanostructures, ISIS, Université Louis Pasteur, Strasbourg, FRANCE.

Metallic films drilled with sub-wavelength holes (~150 nm) can transmit the light with an efficiency thousand times larger than the one that theory predicts for single holes. The efficiency can even be larger than the fractional area of the holes, which means that the light falling beside the holes is going to emerge on the other side of the sample via the apertures. This extraordinary transmission is due to the coupling of the incident light with the surface plasmons of the film. The transmission spectrum contains peaks attributed to surface-plasmon modes that depend on both the symmetry and the 2D lattice parameter. We have shown that this phenomenon remains possible even with a single hole. These results, and others, suggest many applications for this phenomena including sub-wavelength lithography and novel probes for near-field optics.

### 4:30 PM D8.6

HOLOGRAPHIC PHOTOPOLYMERIZATION-BASED TEMPLATING OF NANO-SIZED PARTICLES. C.L. Dennis, AFRL/MLPJ, WPAFB, OH; V.P. Tondiglia, L.V. Natarajan, SAIC/MLPJ, WPAFB, OH; D.W. Tomlin, TMCI/MLPJ, WPAFB, OH; H. Jeon, UDRI/MLBP, WPAFB, OH; R.A. Vaia, T.J. Bunning, AFRL/ML, WPAFB, OH.

Holographic photopolymerization has been extensively utilized in the past to impart information in thin, solid films of pure polymer. The spatially varying intensities caused by constructive and destructive interference result in a modulation of crosslink density and composition which manifests itself as a periodically varying refractive index profile. We have extended this process by dispersing various nano-sized particles including clays, gold colloids, and polystyrene beads in various reactive monomers. The spatially periodic polymerization conditions cause the nano-particles to segregate from the polymer during polymerization with the periodicity dictated by the holographic overlap of the curing laser. Sub-micron length scales are easily obtainable and have been demonstrated with this method. For a clay system, initial measurements using polarization-based optics, HRSEM, and TEM indicate that the clay sheets are aligned and spatially segregated on an 800 nm period. We report here on the initial studies to template a variety of nano-sized particles in various neat and aqueous-based photo-polymerizable monomers.

### 4:45 PM D8.7

SYNTHESIS AND PHOTONIC PROPERTIES OF SUB-MICRON 3-D METALLIC PHOTONIC CRYSTALS WITH CERMET AND NETWORK TOPOLOGY. Anvar A. Zakhidov, Ray Baughman, Ilyas Khayrullin, Igor Udod, Honeywell Technical Center, Morristown, NJ; N. Eradat, J.D. Huang, Alex Efros and Valy Vardeny, Dept. of

Physics, Univ. Utah, Salt Lake City, UT; Mikhail Sigalas, Rana Biswas, Ames Laboratory and Dept of Physics, Iowa State University, Ames, IA.

Highly periodic three-dimensional metallic mesh composites with silica, and highly porous metallic nano-foams have been prepared by micromolding synthetic opals using melts of metals and semimetals. These metallic photonic crystals show photonic and electronic properties, which strongly depend on their topology and geometry. Network topology, created in a form of interconnected spherical cages of 200-400 nm diameter, shows a reflectivity peak in the infrared (IR) spectral range, due to a metallic photonic band gap (MPBG), reminiscent of plasmon edge of bulk metal, which is significantly shifted to longer wavelengths. On the other hand, a discontinuous topology of separated clusters in a matrix (so called cermet topology) obtained by three distinct techniques (by controlling the pressure and temperature of the melt during the infiltration process), do not show MPBG. In the visible spectral range, bright and sharp colors of Bragg scattering are observed from both topologies, which are more intense than in conventional, dielectric gem opals in agreement with computer modeling of light reflection from cermet metallo-dielectric photonic crystals. This metallic PBG structures can be used as novel type IR reflectors, color mirrors and conductive electrodes having properties controlled by the topology of 3-D superstructure. Theoretical model is developed for plasmon excitations in such 3-D structures, which predicts three branches of plasmons and describes the observed features of light reflection in metallic meshes with different connectivities.

SESSION D9: POSTER SESSION  
FABRICATION, CHARACTERIZATION, AND  
APPLICATIONS OF NANOSTRUCTURES

Chairs: John A. Rogers, Lhadi Merhari, Alamgir Karim,  
David J. Norris and Younan Xia  
Thursday Evening, November 30, 2000  
8:00 PM  
Exhibition Hall D (Hynes)

**D9.1**

Transferred to D1.9

**D9.2**

PRECISE CHARACTERIZATION OF ANTIREFLECTIVE COATING AND RESISTS IN THE VUV RANGE FOR 157 NM LITHOGRAPHY. Pierre Boher, Patrick Evrard, Christophe DeFranoux and Jean Louis Stehle, SOPRA SA, Bois Colombes, FRANCE.

Lithography in the VUV range requires precise characterization of photo resists and antireflective coatings as soon as optics in this wavelength range. Due to the reduced thickness of the layers, spectroscopic ellipsometry is certainly the best candidate to obtain precise structural information. Another interesting technique is the grazing x-ray reflectance which provides not only the thickness of the layers but also quantitative information on the interface and surface roughness. SOPRA has developed a combined instrument which allows measurements with both techniques at the same place and combined analysis with the same software. The optical setup of the ellipsometer is especially designed to allow measurements in the VUV range with a real double monochromator directly in the polarizer arm to avoid photo bleaching and the detector, a photo multiplier tube working in photon counting mode, in the analyzer arm. The system is included in a glove box continuously purged from oxygen and water to be able to work in the part per million range. This precaution is absolutely necessary to avoid gas absorption in the VUV range down to 145 nm. The same optical setup can be used to make photometric and scatterometric measurements. An x-ray tube with its collimating optics is also included on one arm of the goniometer, and a monochromator with its x-ray detector on the other side. Grazing x-ray reflectance measurements are then also possible on the same position of the sample. The proposed paper will present in details this new system with measurement results on different kind of photo resists and antireflective coatings for 157 nm lithography.

**D9.3**

A STATE OF THE ART REFLECTOMETER FOR THE CHARACTERIZATION OF LITHOGRAPHIC MASKS AND OPTICS FOR EUV LITHOGRAPHY. Pierre Boher, Stephane Branly, Patrick Evrard, Jean Philippe Piel, and Jean Louis Stehle, SOPRA SA, Bois Colombes, FRANCE.

A commercial table-top soft-ray/EUV reflectometer has been developed for characterization of materials and optics over the range 12-14nm. This instrument is intended to be used as day to day characterization tool for masks and optics for EUV lithography. So,

special attention has been given to the accuracy of the instrument and to the facility of use. The spectral range is 12-14nm with a position accuracy of  $\pm 0.1\text{\AA}$  and a special resolution  $\Delta\lambda/\lambda$  of 1%. The spot size on the sample surface is about  $2\text{mm}^2$ . The angle of incidence can be changed from 5 to  $90^\circ$ . The accuracy on the reflectance is 1% and the repeatability is better than 0.5%. The maximum size of the sample is 200nm. Flat samples can be mapped on the entire surface while curved ones can be measured on one diameter. Transmittance measurements are also possible. The environment is controlled to avoid contamination of the samples and the base pressure in the analysis chamber is less than  $10^{-9}$  torr. Technical details of the system will be presented and first experimental results will be discussed.

**D9.4**

PHOTOCHEMICAL MICROMACHINING OF LYSOZYME CRYSTALS. Orlin D. Velev, Stephen R. Dziennik, Eric W. Kaler, Abraham M. Lenhoff, Dept of Chemical Engineering, Univ of Delaware, Newark, DE.

Three-dimensional protein crystals are widely available, but little studied, self-assembled nanostructured materials. By virtue of the well-defined and compact structure of the protein molecules, and their efficient functionality, e.g. as enzymes or in electron transfer systems, such 3D protein lattices hold promise as biocatalysts, components of biosensors, and for high density memory storage. However, they may be of value only if it is possible to control and manipulate their sizes or shapes, which cannot be done by mechanical machining as the crystals are extremely fragile. As an alternative, we have developed ways to use light to manipulate and micromachine lysozyme crystals infused with fluorescent surfactants. Three complementary effects caused by the interaction of UV/vis light with such crystals are reported. The first is the photochemical degradation of lysozyme in the presence of pyrene. In this case the denatured protein subsequently dissolves and is etched off the crystal. The second is a phenomenon wherein the protein phase can be deposited, moved, or dissolved by collimated light beams. This bears some similarity to the "light tweezers" used to manipulate colloidal particles. Both of these effects could find application in optical micromachining of protein crystals such as etching, drilling, cutting, patterning, or by guided deposition onto substrates. We also show how light-triggered bleaching or photoactivation could be used to record information into the lattice. These photochemical approaches may also be applied to patterning and micromachining of protein layers and hydrogels on sensors and biochips. Refs: Velev, Kaler and Lenhoff, Adv. Mater, 11, 1345 (1999); J. Phys. Chem. B, submitted.

**D9.5**

DIRECT WRITE OF ELECTRONIC CONDUCTOR AND RESISTOR MATERIALS USING A NOVEL LASER TRANSFER TECHNIQUE. Rohit Modi, The George Washington Univ., Dept. of Mechanical and Aerospace Engineering, Washington, DC; H.D. Wu, SFA, Inc., Largo, MD; A. Pique, R.C.Y. Auyeung, Naval Research Laboratory, Washington, DC; S. Lakeou, Univ. of District of Columbia, Washington, DC; D.B. Chrisey, Naval Research Laboratory, Washington, DC.

MAPLE direct write (MAPLE DW) is a new laser-based direct write technique which combines the basic approach employed in laser induced forward transfer (LIFT) with the unique advantages of matrix assisted pulsed laser evaporation (MAPLE). The technique utilizes a laser transparent substrate with one side coated with a dilute matrix consisting of the material to be transferred mixed with an organic binder and/or precursor. As with LIFT, the laser is focussed through the transparent substrate onto the matrix coating. When a laser pulse strikes the coating, the matrix absorbs laser light and aids in transferring the material of interest to an acceptor substrate placed parallel to the matrix surface. MAPLE DW is a maskless deposition process designed to operate in air and at room temperature, that allows for the generation of complex patterns with micron scale linewidths. With MAPLE DW, diverse materials such as metals and polymer-conductor composites have been successfully transferred onto various types of acceptor substrates. The various structures produced by MAPLE DW were characterized using 3-D surface profilometry, scanning electron microscopy and x-ray diffraction. The electrical resistivity measurements of the silver metal lines and polymer-conductor composite resistors were done using an impedance analyzer. An overview of the key elements of the MAPLE DW process including our current understanding of the material transfer mechanism as well as its capabilities and current limitations as a rapid prototyping technique will be presented. This work was supported by DARPA, through the DARPA-MICE program and the Office of Naval Research.

**D9.6**

RAPID PROTOTYPING OF OPTICALLY PROGRAMMABLE PHOTSENSITIVE THIN-FILM NANOSTRUCTURES. Dhaval A. Doshi<sup>1</sup>, Hongyou Fan<sup>1</sup>, Shawn Coffee<sup>1</sup>, Darren R.

Dunphy<sup>3</sup>, Nicola K. Huesing<sup>2</sup>, Alan J. Hurd<sup>3</sup>, C. Jeffrey Brinker<sup>1,3</sup>.  
<sup>1</sup>University of New Mexico, Albuquerque, NM; <sup>2</sup>Vienna University of Technology, Vienna, AUSTRIA; <sup>3</sup>Sandia National Laboratories, Albuquerque, NM.

Control of structure and function on multiple length scales is evident in Nature and crucial to advances in micro- and nanotechnologies. Cooperative self-assembly processes of inorganic species and amphiphilic molecules afford an efficient means to build nano-structures and nanocomposites. Thin films are perhaps the most promising applications of so-called mesostructured materials, and the ability to build hierarchical structures and functionality is the key to their successful implementation in future micro-systems. To date, so-called micro-contact printing and micro-molding in capillaries techniques have been used to create patterned thin-film silica mesophases. Recently we have demonstrated the use of self-assembling 'inks' in rapid patterning of organo-functionalized thin-film mesophases with pen lithography, ink-jet printing, and selective de-wetting. We have also developed a novel lithographic procedure that not only enables selective etching of photosensitive silica mesophases (thereby serving as a 1-step negative resist process), but more importantly allows optical definition and control of thin-film mesostructure (hexagonal v/s cubic) and properties. The process has a unique capability of continuous control of thin-film properties i.e. refractive index, pore size and wetting behavior. Incorporation of a photoacid generator into the self-assembling 'ink' allows us to exploit the pH sensitivity of the supra-molecular self-assembly by affecting the silica condensation kinetics and also the mesophase formation. The use of lithography in conjunction with the non-lithographic patterning technique allows control of structure and function on multiple length scales facilitating the fabrication of photonic and fluidic devices. This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000 and the DOE BES program. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

#### **D9.7**

**STRUCTURED DEPOSITION OF NANOMETER-SIZED AEROSOL PARTICLES ON SILICON OXIDE.** Thomas J. Krinke, Heinz Fissan, Process- and Aerosol Measurement, Gerhard-Mercator-University Duisburg, Duisburg, GERMANY; Knut Deppert, Martin H. Magnusson, Lars Samuelson, Solid State Physics, Lund University, Lund, SWEDEN.

If nanometer sized metal and semiconductor particles are to be used as components in future photonic or quantum electronic devices, this will require not only deposition but also ordered positioning of nanoparticles on a substrate. We have developed a procedure for arranging chains of nanometer-sized particles on oxidized silicon substrates by direct deposition from the gas phase of an aerosol. The particles were attracted to charge patterns created on the insulator surface by contact charging; metal is pressed against the surface and charges then remain in the oxide for several hours. As substrates, we used thermal wet oxidized p silicon. After the charge patterning, singly charged indium aerosol particles with a diameter of 30 nm were deposited. Due to the surface treatment and the high mobility of the particles, the deposition is highly selective and the particles are collected on the surface charges. We were able to create lines of particles as narrow as 100 nm in width and with lengths of several millimeters. Since it is possible to create structures with resolutions in the millimeter size range, a connection between the macroscopic and the nanoscale could be possible to make in one process step. Our approach opens the possibility to create patterns composed of nanometer-sized particles, with a resolution better than conventional optical lithography, by the simple deposition of charge patterns on a substrate.

#### **D9.8**

**A NEW ASSEMBLING METHOD FOR NANOSIZE PARTICLES USING AN ELECTRIFIED PATTERN DRAWN BY AN FOCUSED ION BEAM.** Hiroshi Fudouzi, Mikihiko Kobayashi and Norio Shinya, National Research Institute for Metals, Tsukuba, JAPAN.

This paper will demonstrate a new technique to fabricate a two-dimensional microstructures with nanosize particles. Nanosize particles attract much attention because of their unique properties unlike bulk properties. Micro- and nano- structures assembled with nano-size particles have potential applications in electronical, optical and bio-chemical fields. One method of fabricating such structures is through the assembly of nano-sized particles. Micropatterned particle assemblies have been produced with lithographically patterned electrodes. Patterned SAM(Self-assembly mono-layer) films or micromolds methods are also used. We proposed a new method to assemble nanosize particles on a substrate without the films or the molds. In this paper the detail of the technique is described and results of experiments, using TiO<sub>2</sub> (21nm in diameter) particles, are

presented. N-type (100) Si wafer having an oxidizing layer of 990nm thickness was used as a substrate. A focused ion beam (Ga<sup>+</sup>-FIB) with 30keV scanned on the substrate. The spot size of the FIB is approximately 0.1 $\mu$ m. Positively electrified pattern with a dose of  $2.5 \times 10^{13}$ /cm<sup>2</sup> was formed on the substrate. Titanium oxide (TiO<sub>2</sub>) particles were dispersed into an ethanol to form a colloidal suspension. The substrate with the electrified pattern was immersed in the colloidal suspension for 12hr. The TiO<sub>2</sub> particles were attracted to the electrified pattern and deposited on it. Then the substrate was rinsed with an ethanol and dried it in air. The TiO<sub>2</sub> particles deposited on the substrate was observed with an optical microscope in dark field mode. The particles on the substrate formed two-dimensional microstructures corresponding to the electrified pattern. This method enables to form micro-structure assembled with nano-sized particles. We believe that the technique is also applicable to fabricate nano-structures.

#### **D9.9**

Transferred to D1.2

#### **D9.10**

**NI-Fe-BASED NANO-STRUCTURE FOR SPIN TUNNELING DEVICES FABRICATED BY ATOMIC FORCE MICROSCOPE.** Yasushi Takemura, Yokohama National University, JAPAN; Jun-ichi Shirakashi, Akita Prefectural University, JAPAN.

Lithography techniques using scanning probe microscopes have attracted much interest as novel tools for fabricating electron devices with well defined structures of a nano-meter scale. NiFe- and Ni-based nano-structures fabricated by atomic force microscope (AFM) are reported in this paper. Metals are oxidized with applying a negative bias on the AFM tip. This anodic oxidation process is an electrochemical reaction between metals and water in air. The selectively oxidized region can be utilized as a potential barrier of planar-type spin tunneling devices. NiFe and Ni thin films of 3-20 nm thickness deposited by a sputtering on SiO<sub>2</sub>/Si substrates were selectively oxidized using AFM. NiFe- and Ni-oxide dots and wires with 40-140 nm size were obtained. The dot size and wire width could be controlled by changing the bias voltage from -6 to -50 V. Patterned structures consisting of metal and its oxide were also fabricated by scanning the AFM tip. The junction area of planar-type device fabricated by this method can be as small as a few nm (film thickness) by 100 nm (sweep length), which can not be achieved by conventional optical or electron beam lithography. The small junction area is expected to realize a room temperature operation of single electron tunneling devices and other quantum phenomenon. Ni/Ni-oxide-based planar-type MIM diode was fabricated as an example of nano-structured spin tunneling devices. The current-voltage characteristic was dominated by a leak current and a rectification was not observed, which should be improved by the film deposition method and by optimizing parameters on AFM oxidation. Based on these results, a couple of novel spin tunneling devices including single electron tunneling device and magnetic random access memory (MRAM), and their fabrication methods are also discussed.

#### **D9.11**

**SELF ARRANGEMENT OF SUBMICRON PORES AND MODULATION OF THEIR DIAMETER IN ANODICALLY-ETCHED n-InP.** I.M. Tiginyanu, S. Langa, Technical Univ of Moldova, Laboratory of Low-Dimensional Semiconductor Structures, Chisinau, MOLDOVA; J. Carstensen, M. Christophersen, H. Föll, Christian-Albrechts Univ, Materials Science Dept, Kiel, GERMANY.

Over the last years, porosity emerged as an effective tool for engineering the properties of semiconductors. In particular, two-dimensional infrared photonic band gap material was successfully fabricated on crystalline Si by using electrochemical etching technique[1], the ordered distribution of pores being defined by photolithography. The shift from semiconductor element to compound entails considerable crystallographic change and, in consequence of this, pronounced anisotropy of wet etching. In this work we show that anodic etching of (100)-oriented n-InP crystalline substrates in HCl-based electrolytes results in the formation of porous structures with different morphologies. At low current densities the pores prove to grow along (111) crystallographic directions and they possess a well-defined triangular shape. At high anodic current densities the morphology of pores reflects the current flow during the anodization process; such pores are called current-line oriented ones. A self arrangement of submicron pores was observed in n-InP under certain conditions of electrochemical etching. Besides, self-induced voltage oscillations were observed during anodic etching of highly and moderately doped substrates at high constant current densities. The oscillations involved were found to lead to a synchronous modulation of the diameters of all pores in the sample. The physical and electrochemical processes responsible for the occurrence of voltage oscillations are discussed. The self-controlled etching process involved proves to be suitable for three-dimensional micro- and nano-

structuring of n-InP and therefore promising for elaborating novel structures exhibiting high spatial variations of the dielectric properties. [1] U. Grönning et al.: Appl. Phys. Lett. 58 (1996) 747.

#### **D9.12**

STM STUDY OF ANNEALING EFFECTS ON Si NANO *pn* JUNCTIONS FABRICATED BY ION IMPLANTATION.

Toshiiko Okui, Shigehiko Hasegawa, Hisao Nakashima, Osaka Univ, The Institute of Scientific and Industrial Research, Osaka, JAPAN; Hidenobu Fukutome, Takayuki Aoyama, Hiroshi Arimoto, Fujitsu Laboratories Ltd, Kanagawa, JAPAN.

Since semiconductor devices have been miniaturized to improve their performance, it is important to characterize structures and electrical properties on a nanometer scale. As for MOS structures, since the channel length of the MOS structure has shrunk, the diffusion of impurities during annealing strongly affects the structure and the local electrical properties. Recently, we have used scanning tunneling microscopy/scanning tunneling spectroscopy (STM/STS) to characterize the electrical and electronic properties of nano *pn* junctions formed on Si(001) surfaces. It is reported that three different regions of n-type, p-type, and depleted regions can be visualized with STM. In this work, annealing effects on ion implanted Si nano *pn* junctions are examined and are discussed in terms of the local carrier concentration and diffusion of implanted impurities. Planar nano *pn*<sup>+</sup> junctions were fabricated on Si(001) substrates covered with SiO<sub>2</sub> by B and As ion implantation and electron beam lithographic technique. Then, annealing at 800°C for various times was carried out to activate implanted impurities. It is observed from the STM images that the width of depleted regions increases with the increase of the annealing time. Assuming an abrupt *pn*<sup>+</sup> junction, the extension of the depleted region results from the decrease of carrier concentration in the p-type region beneath SiO<sub>2</sub> layers. There are two explanations of the variation observed in the carrier concentration. One is carrier compensation resulting from the diffusion of As into p-type regions through the SiO<sub>2</sub>/Si interface, and the other is the decrease of carrier concentration due to B diffusion into SiO<sub>2</sub> layers. To make a definitive conclusion, we fabricated similar nano *pn* junctions by varying the sequence of B ion implantation, As ion implantation and annealing. From the comparative STM study of these samples, it is considered that the As diffusion through the SiO<sub>2</sub>/Si interface is dominant.

#### **D9.13**

ELECTROPHORETIC DEPOSITION OF LATEX-BASED 3D COLLOIDAL PHOTONIC CRYSTALS: A TECHNIQUE FOR RAPID PRODUCTION OF HIGH QUALITY OPALS.

Dmitry S. Koktysh, Oklahoma State Univ, Dept of Chemistry, Stillwater, OK; Andrey L. Rogach, Univ of Hamburg, Inst of Physical Chemistry, Hamburg, GERMANY; John W. Ostrander, Nicholas A. Kotov, Oklahoma State Univ, Dept of Chemistry, Stillwater, OK.

Three-dimensional colloidal crystals have been grown by electrophoretic deposition on conducting ITO glass supports from aqueous-ethanol colloidal solutions of monodisperse submicrometer-sized negatively charged polystyrene latex spheres in a dc field. The technique offers the possibility to produce uniform single-crystal colloidal multilayers on the time scale of minutes, which is a drastic acceleration in comparison with the gravity sedimentation technique that needs weeks or even months. SEM and AFM images of colloidal crystals reveal that close-packed 3D fcc ordering of the latex spheres extends over large areas. Electrophoretically deposited colloidal crystals were brightly colored in both transmitted and reflected light because of the optical diffraction on regular multilayers and show a pronounced photonic stopband in the visible spectral range in the normal incidence transmission spectra with a position depending on the size of latex spheres. The position of the dip in the transmission spectrum can be tuned accurately through the particles size control. The electrophoretic deposition has also been used for the impregnation of 3D colloidal crystals with luminescent CdTe nanocrystals. The luminescence spectrum of CdTe nanocrystals shows a dip at the wavelengths corresponding to the spectral position of the photonic stopband of the colloidal crystal due to the overlap of the photonic stopband and the spectrum of spontaneous emission of the nanocrystals. This phenomenon represents both fundamental and practical importance for the design of photonic devices.

#### **D9.14**

MANIPULATION OF COLLOIDAL CRYSTALLIZATION FOR PHOTONIC APPLICATIONS BY HIGH AND LOW FREQUENCY ELECTRIC FIELDS. Alfons van Blaaderen, Anand Yethiraj, FOM Inst. AMOLF, Amsterdam / Condensed Matter Dept., Debye Inst., Utrecht University, Utrecht, THE NETHERLANDS.

Electric fields applied to non-conducting particle suspensions have until now mainly been used to manipulate the viscosity, hence the term: electro-rheological fluids. In this contribution we show that these fields at low frequencies can also be used in photonic crystal

applications e.g., to switch face centered cubic crystals into body centered tetragonal crystals on a millisecond time scale. Using the same fields it is also possible to create non-close packed colloidal crystalline arrangements by using a template of particles first attached to the transparent electrodes. These template particles were positioned on the electrodes by means of electric fields at high frequencies: a pair of optical tweezers. Finally, we show how electric fields at low frequencies and applied in a plane perpendicular to gravity leads to an interesting set of layer transitions, again from FCC to BCT. This field configuration can also be used to anneal out defects in the creation of large FCC crystals.

#### **D9.15**

FABRICATION OF MICRO- AND NANOSTRUCTURES WITH MONODISPERSED COLLOIDAL SPHERES AS THE ACTIVE COMPONENTS. Byron Gates, Yadong Yin, Younan Xia, Univ of Washington, Dept of Chemistry, Seattle, WA.

Monodispersed colloidal spheres with dimensions in the range of 10 nm - 10 μm can be used as building blocks to fabricate highly ordered 3D micro- and nanostructures. For example, they can be self-assembled into closely packed lattices which can be subsequently used as templates to generate 3D porous structures. In this presentation, we will discuss the recent progress in our groups regarding this approach.

#### **D9.16**

ELECTRODEPOSITION OF THREE-DIMENSIONAL METAL MESHES WITHIN OPAL MEMBRANES. Lianbin Xu, Weiie L. Zhou, Amar Kumbhar, Christoph Frommen, Charles J. O'Connor, John B. Wiley, Department of Chemistry and the Advanced Materials Research Institute, University of New Orleans, New Orleans, LA; Ray H. Baughman, Anvar A. Zakhidov, Honeywell Int., Corporate Technology, Morristown, NJ.

Electrochemical methods have been used to deposit metals (such as nickel, cobalt and gold) within porous opal membranes. The opals themselves consist of close-packed silica beads whose void space acts as a mold for the growth of the metal arrays. Subsequent dissolution of the opal produces open three-dimensional metal mesh structures. Details on the preparation and characterization of these materials are presented including electron microscopy and magnetic studies.

#### **D9.17**

NOVEL COLLOIDAL ASSEMBLY METHODS FOR THE PREPARATION OF CORE-SHELL COMPOSITE MATERIALS. Michael S. Fleming, Tarun K. Mandal, David R. Walt, The Max Tishler Laboratory for Organic Chemistry, Tufts University, Department of Chemistry, Medford, MA.

Colloidal assembly is a process by which particles ranging in size from nanometers to micrometers are organized into structures by mixing two or more particle types. Assembly is controlled by either specific or non-specific interactions between particles. Examples include chemical bonding, biological interactions, electrostatic interactions, capillary action and physical absorption. The assembly process is performed such that smaller particles assemble around larger ones. In this paper, we report on colloidal assembly of polymer nanoparticles (50-300 nm diameter) onto silica particles (3-10 micron diameter) using specific chemical (amine-glutaraldehyde) or biological interactions (avidin-biotin). Heating the assembled materials to temperatures above the glass transition (T<sub>g</sub>) of the polymer nanoparticles allows the polymer to flow over the microsphere surfaces resulting in uniform core-shell materials. Polystyrene and poly (methyl methacrylate) nanospheres were used to produce such materials. Shell composites were created by mixing both nanosphere types prior to assembly/ melting. The materials presented in this paper were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and FTIR spectroscopy.

#### **D9.18**

POLYELECTROLYTE MULTILAYERS AS SOFT TEMPLATES FOR INORGANICS: CONTROLLING INORGANIC CONCENTRATION. Tom C. Wang, Robert E. Cohen, MIT, Dept of Chemical Engineering and Center for Materials Science and Engineering, Cambridge, MA; Michael F. Rubner, MIT, Dept of Materials Science and Engineering and Center for Materials Science and Engineering, Cambridge, MA.

We have previously demonstrated that polyelectrolyte multilayers (PEM) can be used as nanoreactors to template the in-situ formation of various inorganic particles, including metals like silver and semiconductors like lead sulfide. PEM fabricated from poly(allylamine hydrochloride) and poly(acrylic acid) contain free carboxylic acid groups that can bind various inorganic ions by ion-exchange. The ions are subsequently converted to particles, by reduction for example. With heterostructure multilayers, incorporating poly(sodium

4-styrenesulfonate) into the PEM, nanoscale spatial control over the nanoparticles is achieved. Now, we demonstrate a strategy for controlling the amount of nanoparticles of palladium, silver, and gold prepared in-situ within the PEM. Using an iterative ion-exchange and reaction scheme, the inorganic content within the PEM can be increased. With UV-vis spectroscopy, TEM, and impedance spectroscopy, the silver content within the PEM is monitored over successive ion-exchanges and reductions of silver cations, showing increased silver concentration and size. The continued growth in size and concentration of particles can continue to be confined within select regions of the PEM. Alternatively, electroless metal deposition chemistries can be used to increase metal content within the PEM. In-situ prepared gold nanoparticles are used to catalyze the electroless deposition of gold while palladium nanoparticles are used to catalyze copper or nickel deposition.

#### **D9.19**

**NEW SIMPLE METHOD FOR FABRICATION OF FINE METAL PATTERNS.** Yasuyuki Hotta, Toshiro Hiraoka, Koji Asakawa, Shigeru Mataka, Toshiba Corp., Corporate R&D Center, Kawasaki, JAPAN.

We have developed a new, simple method to fabricate fine metal patterns at room temperature. Electroless plating has the advantages of lower cost and processing temperature compared with conventional methods such as sputtering, but it is difficult to form fine patterns on substrates by etching. We have proposed a new, simple patterning method using electroless plating without etching. It can be attained by forming hydrophilic and hydrophobic patterns on the substrates. A thin layer of photo-sensitizers was coated on the substrates, which were exposed to UV lights using a photo mask. In the exposed areas, the photo-sensitizers generate hydrophilic groups such as carboxyl groups by photo-reactions. They act as cation exchange groups and adsorb metal ions in the ion-exchange reaction. The adsorbed metal ions are changed into metallic particles by the reduction, and they can act as a catalyst for the electroless plating. In the experiment, it was observed that metal ions were adsorbed on carboxyl groups. The metal catalyst formed on the exposed areas by reduction treatment, and the sample was immersed in an electroless copper plating solution. Copper was selectively deposited by the self-catalyst mechanism according to the exposure patterns. As a result, micrometer-scale copper patterns could be fabricated on the substrate. This technique is also effective when metals are deposited into the submicron holes. It can be applied as interconnecting lines for electronic and photonic devices. Moreover, a wide variety of applications can also be anticipated.

#### **D9.20**

**DIRECT SURFACE PATTERNING BY LASER-INDUCED LOCALIZED CHEMISTRY.** Aurelie Lachish-Zalait, David Zbaida, Eugenia Klein, Michael Elbaum, Weizmann Institute of Science, Dept of Materials and Interfaces.

We describe a method for direct-write lithography by localized, laser-induced chemical reduction of soluble reagents and their precipitation onto a surface. A single-mode infrared laser diode (830 nm, 200 mW) is focused by a high-power microscope objective into a homogeneous solution, in an arrangement similar to "optical tweezers". Rather than collecting preformed colloids, the laser induces precipitation of the product directly from solution. The reaction is self-sustaining and fast if the product absorbs the laser wavelength, generating a localized heating. Continuous lines or patterns are drawn by moving the stage, or by scanning the beam. Metallic silver was deposited from a basic solution of diamminesilver hydroxide  $\text{Ag}(\text{NH}_3)_2\text{OH}$ . Scanning electron microscopy shows a "palm-leaf" morphology. Energy dispersion analysis (EDS) confirms the composition of Ag metal, and lines are electrically conductive. Reaction with thiol- or bromine-containing compounds generates the appropriate chemical modifications. Inclusion of capping agents in the solution before deposition regulates the morphology, width (between 0.7 and 10 microns), and conductivity of the deposits. The process has also been demonstrated for Au and Cu. (The latter is produced in oxide rather than metallic form.) Preliminary work with tetrathiomolybdate  $(\text{NH}_4)_2\text{MoS}_4$  solution has yielded patterns of  $\text{MoS}_2$ , indicating that the method is not limited to metals, and may find broad application in the patterning of materials not suited to standard lithographic processing. Particular advantages to this laser-based lithography are in the ease of prototyping without a mask, of producing sample-specific markings (e.g. serial numbers), and of building multi-component structures simply by exchanging the solution. The method shows potential for simple production of micron-scale metal-semiconductor junctions with minimal equipment overhead. The generation of a fresh surface deposit, followed by its specific functionalization and blocking, also provides a convenient means for sequential generation of chemical or biochemical arrays.

#### **D9.21**

**OPTICAL PATTERNING OF PHOTSENSITIVE THIN-FILM SILICA MESOPHASES.** Dhaval A. Doshi<sup>1</sup>, Nicola K. Huesing<sup>2</sup>,

Mengcheng Lu<sup>1</sup>, Hongyou Fan<sup>1</sup>, Kelly Simmons-Potter<sup>3</sup>, Barrett G. Potter, Jr.<sup>3</sup>, Alan J. Hurd<sup>3</sup>, C. Jeffrey Brinker<sup>1,3</sup>. <sup>1</sup>University of New Mexico, Albuquerque, NM; <sup>2</sup>Vienna University of Technology, Vienna, AUSTRIA; <sup>3</sup>Sandia National Laboratories, Albuquerque, NM.

Cooperative self-assembly processes of inorganic species and amphiphilic molecules have experienced major advances over the past eight years. A variety of macro- and microstructures have been synthesized such as powders, fibers, monoliths, thin films, hollow and transparent hard spheres and aerosol particles. Thin films are perhaps one of the most promising applications of so-called mesostructured materials, and the ability to build hierarchical structures and functionality is the key to their successful implementation in future micro-systems. Recently, various non-lithographic techniques such as micro-contact printing, micro-molding in capillaries, ink jet printing, selective de-wetting, and micro-pen writing have been used to create patterned thin-film silica mesophases. Lithographic and other patterning techniques demonstrated so far define regions where a film is present or not. Here we report a lithographic procedure that enables selective etching of photosensitive silica mesophases. The process not only provides a general technique to prepare patterned mesoporous silica without photoresists, molds, or stamps. More importantly it allows optical definition and control of thin film mesostructure (e.g. hexagonal v/s cubic) and properties such as refractive index, pore size, surface area, and wetting behavior, rather than merely presence or absence of the film in a pattern. The process involves incorporation of a photoacid generator in the coating sol. Dip/spin coating results in the formation of a photosensitive mesostructured thin film. Selective UV exposure through a mask results in localized acid generation. We exploit the pH sensitivity of supra-molecular self-assembly to control the kinetics of silica condensation and mesophase formation, thereby affecting optical patterning of structure and functionality in the film. The ability to define optically and to control continuously both structure and function on the macro- and mesoscales is of interest for sensor arrays, nano-reactors, photonic and fluidic devices, and low dielectric constant films. More importantly, it extends the capabilities of lithography from conventional patterning by subtractive etching to spatial control of film structure and properties. This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000 and the DOE BES program. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

#### **D9.22**

**3D VOLUME IMAGING OF POLYMERIC NANOSTRUCTURES.** R. Magerle, M. Konrad, A. Knoll, N. Rehse, and G. Krausch, Physikalische Chemie II, Universität Bayreuth, Bayreuth, GERMANY.

Nanotomography is a general procedure for volume imaging with scanning probe microscopy (SPM). As an example we imaged with about 10 nm resolution the three-dimensional (3D) spatial microdomain structure of poly(styrene-*block*-butadiene-*block*-styrene) (SBS) and other polymeric nanostructures. The specimen was eroded step by step by plasma etching and its chemical composition in layers beneath the original surface was imaged with tapping mode scanning force microscopy. Similar to computed tomography, the 3D distribution of polystyrene and polybutadiene (in case of SBS) can be reconstructed from a series of images. This approach might provide a simple means for nanometer (and even atomic) resolution real-space volume imaging of various materials and physical properties. With the success of SPM in mind, volume imaging by SPM promises new insights into the physics of condensed matter on a nanometer scale.

#### **D9.23**

**MULTIPLE PATTERNING OF FUNCTIONAL NANOSTRUCTURES.** Hongyou Fan, Dhaval A. Doshi, Darren Dunphy, Nicola K. Husing, Alan J. Hurd, C. Jeffrey Brinker, Sandia National Laboratories, Catalysis and Porous Materials Department, Albuquerque, NM; University of New Mexico/NSF Center for Micro-Engineered Materials, Albuquerque, NM; Institute of Inorganic Chemistry, Vienna University of Technology, Vienna, AUSTRIA.

The ability to define and control both structure and function on multiple length scales and locations is of interest for microelectronics, sensor arrays, wave guides, photonic and microfluidic devices (Fan, H. et al. Nature, 405, 56-60, 2000). In this presentation, using a self-assembling "ink", we combine a variety of rapid patterning techniques such as ink-jet printing, micro-pen writing, and selective de-wetting to form functional nanostructures in seconds through computer-aided design. In addition, we produce secondary functional patterns within the primary patterns formed by above techniques using photosensitive ink. Finally an aerosol process will be discussed to form patterned functional nanostructures by masks.

#### **D9.24**

**NON-LITHOGRAPHIC VERTICAL NANOCOLUMN ARRAY**

FABRICATION WITH APPLICATION TO FIELD EMITTERS. Michael J. Colgan, Michael J. Brett, University of Alberta, Dept of Electrical and Computer Engineering, Edmonton, AB, CANADA.

A non-lithographic method of fabricating high-density arrays of nanometre-scale vertical columns was investigated. The use of oblique deposition techniques allows the fabrication of isolated vertical columns in a single-step evaporation process without the need for either pre- or post-deposition lithographic processing. Extreme oblique incidence deposition with computer controlled substrate motion was utilized to fabricate column densities exceeding  $10^9 \text{ cm}^{-2}$  and column diameters near 30 nm. The desired column geometry may be engineered through choice of deposition angle and substrate spin rate, with resulting average film porosities near 60%. Periodic nanocolumn arrays have been fabricated utilizing an additional pre-deposition nucleation step. In one potential application of these microstructures, arrays of vertical columns were fabricated from silicon and carbon and tested for field emission characteristics. Further studies will be presented on the use of ion milling to modify the tips of the nanocolumns in order to improve the field emission properties.

#### D9.25

NEW METHOD FOR FIRST PRINCIPLES MODELING OF ELECTRON TRANSPORT THROUGH NANO-ELECTRONIC DEVICES. Mads Brandbyge, Kurt Stokbro, Mikroelektronik Centret, Technical University of Denmark, Lyngby, DENMARK; Jorge L. Mozos, Pablo Ordejón, Institut de Ciència de Materials de Barcelona - CSIC Campus de la U.A.B., SPAIN.

The recent progress in the synthesis and contacting of nanoelectronic devices has opened up possibilities for experimental studies of electron transport through a large variety of nanostructures. To obtain a fundamental understanding of the observed phenomena it is desirable to have reliable theoretical methods for modeling the electron transport. In this paper we will present a new theoretical method for modelling electron transport through nanostructures under non-equilibrium conditions. The electronic structure of the nanostructures are modelled from first principles and are described self-consistently under the non-equilibrium conditions by means of a Green's function technique. Applications of the method to electron transport through gold nanowires and organic molecules attached between the wires will be presented.

#### D9.26

TUNNELING ELECTRON INDUCED LIGHT EMISSION FROM PORPHYRIN MOLECULES. Z.-C. Dong, D. Fujita, T. Ohgi, T. Yakabe, H. Nejoh, National Research Institute for Metals, Tsukuba, JAPAN; T. Terui, S. Yokoyama, M.-N. Zhou, N. Mashiko, Communication Research Laboratory, Kobe, JAPAN; T. Okamoto, RIKEN (Institute of Physical and Chemical Research), Wako, JAPAN.

The electronic feature of the free-base- or Cu-TBP porphyrin is the  $18-\pi$ -electron aromatic system delocalized along the inner 16-membered ring of the molecule. This electronic structure is believed to be responsible for its optical behavior. Indeed, the optical absorption spectrum of porphyrins is successfully rationalized by Gouterman's four-orbital model. This simple model gives rise to a relatively weak (pseudoparity-forbidden) Q-band in the visible region and an intense (optically allowed) Soret or B-band in the near-UV. These features are nicely reproduced in the optical absorption spectra of Cu-TBP porphyrin with the small Q-band at 539.6 nm (2.3 eV) and the sharp B-band at 417.0 nm (3.0 eV). In an effort to understand the photon emission processes of porphyrins by electrons at molecular scale and thus to improve the quantum efficiency of molecular light emission and eventually to explore the feasibility of single molecules in molecular electronics, we have recently initiated an investigation of porphyrin molecules bound onto a metal surface. When an STM tip is positioned above a molecule and a negative tip bias is applied, a net tunneling current flows from the tip to the substrate via the adsorbed molecule. In addition to the excitation of local surface plasmons on the metal substrate, the molecule is also excited by the coupling of molecular electronic states with the local electromagnetic modes and then decays to the ground states with emission of light. The photon intensity is in an approximate linear relation with the input tunneling current, while the bias voltage dependence shows not only a threshold around 1.8 eV, but also a non-linear jump-like structure. When the excitation energy is below ca. 3.0 eV, the photon emission arises primarily from the radiative decay of tip-induced surface plasmon from the metal substrate. However, even under such condition, the effect of molecular enhancement is evident although the mechanism of enhancement has not yet been well understood. Above 3.0 eV, molecular fluorescence starts to contribute significantly to the photon emission. The fluorescence peak exhibits a complex envelope of vibrational bands with the shoulder-peak spacing of 0.1 eV. These observations suggest that, although the excitation mechanism of molecules by electrons might be different from that by photons, the energy absorption behavior appears similar on the basis of the energy

dependence of the optical spectra by electrons and its comparison with the optical absorption spectra of the molecule. In addition to the porphyrin monomers, results on porphyrin dimers and longer oligomers will also be presented. The emission mechanism via inelastic electron tunneling will be discussed.

#### D9.27

Abstract Withdrawn.

#### D9.28

NANOLITHOGRAPHY ON ELECTRON BEAM RESIST TRIMMING TECHNIQUE. Hirohisa Taguchi, Tsutomu Iida, Yoshifumi Takanashi, Science University of Tokyo, Dept of Faculty of Industrial Science and Technology, Chiba, JAPAN; Tatsuro Maeda, Kenichi Ishii, Hiroshi Hiroshima, Eiichi Suzuki, Electrotechnical Laboratory, Electron Devices Division, Nanosilicon Devices Lab, Tsukuba-shi, Ibaraki, JAPAN.

Nanolithography has received much attention for future nanometer-scale devices. In electron beam lithography, the SAL601 chemically amplified negative resist is known to have high resolution, high sensitivity and high dry-etching durability. We have investigated the resist-trimming technique of the SAL601 negative resist to realize ultra-fine patterns which cannot be resolved by the direct electron beam lithography. The 160nm-thick SAL601 resist was coated on a sample wafer. The soft bake step was performed at 120°C for 1min. The sample was then exposed by using a 50kV electron beam lithography system. Designed linewidth were from 40 to 100nm and electron dose was 40-200  $\mu\text{C}/\text{cm}^2$ . Following the post exposure bake (100°C, 1min), the resist was developed for 2min by immersing in the MF622 developer. A barrel type plasma etcher was used to trim the patterned resist isotropically with an oxygen pressure of 1245mTorr and a RF power of 200W. The resist profiles were evaluated by SEM observation. The fine rectangular resist patterns have been obtained with the electron dose of 150  $\mu\text{C}/\text{cm}^2$ . The measured linewidth is about 16nm wider than the designed linewidth (40-100nm). The resist patterns have been trimmed for 150sec. In the case of the designed linewidth of 40nm, the film thickness is reduced from 160nm to 130nm and the linewidth decreases from 57nm to less than 20nm. By isotropic resist trimming with approximately 18nm, the ultra-fine resist patterns have been successfully fabricated with the high-aspect-ratio of more than 6. We confirm that the trimmed resist with less than 20nm is successfully transferred to the poly-silicon layer using reactive ion etching (RIE). This resist process is applicable to nanometer-scale device fabrication.

#### D9.29

SUB 100 NM PATTERNING OF ALUMINUM FILM BY AFM LOCAL OXIDATION. Andrea Notargiacomo, Vittorio Foglietti, Florestano Evangelisti, Unit INFN, Dipartimento di Fisica E. Amaldi, Universita' di Roma Tre, Rome, ITALY and Istituto di Elettronica dello Stato Solido - CNR, Rome, ITALY. Giovanni Capellini, Univ of Roma.

Scanning-probe-assisted lithography is a valid method to achieve a patterning resolution below 100 nm: at lower cost respect to e-beam microfabricator, scanning microscope systems provide optimal resolution and positioning accuracy, but also lower throughput. Several techniques to induce modification on a sample surface were successfully developed showing good results. Among them the local oxidation is one of the most attractive. By applying a negative probe-to-sample bias, both semiconductors and metals can be oxidized at a nanometer scale. We report our results in fabricating aluminum and aluminum oxide masks starting from an aluminum film deposited on silicon and silicon dioxide substrates. An atomic force microscope probe is used to locally anodize aluminum and wet etching serves to remove the unwanted material. Therefore, a thin aluminum film can be used as a conventional resist that is locally exposed to the electric field induced by the probe. Positive/negative masks can be obtained by respectively removing the exposed/unexposed regions using highly selective etching solutions at room temperature. Aluminum based masks are MOS compatible and are suitable to sustain dry etching processes using fluorinated gases mixtures. We report examples of sub-100 nm pattern transfer on Si, SiO and SiGe substrates using the AFM fabricated masks. Differences in anodization behavior of sputtered and e-beam evaporated aluminum are also reported.

#### D9.30

SURFACE MORPHOLOGY AND ORDERING OF ULTRATHIN SMECTIC LC DIBLOCK COPOLYMER FILMS. Jung-Sheng Wu, Dept of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA; Michael J. Fasolka, Sushil K. Satija, National Institute of Standards and Technology, Gaithersburg, MD; Paula T. Hammond, Dept of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA.

The morphology of side chain liquid crystalline (LC) diblock

copolymers has been examined as thin films with thickness from half to twice of the of the block copolymer period. Due to the wetting properties of the LC diblock copolymer, LC terraces are observed on the top surfaces corresponding to the single smectic layer spacing. Holes and islands equal in depth to the block copolymer period are also observed; however, both blocks coexist on the surfaces to form mixed layers. SAXS, TEM, XPS, AFM, and X-ray specular reflectivity have been used to determine the complex morphology and LC orientation. LC anchoring is planar at the substrate; but homeotropic anchoring at the air surface is seen in both homo and block copolymers. It is thought that this anchoring causes the terraced surface morphology. The chain arrangement of top homeotropic LC layer is also proposed by 2-D simulation and surface tension calculation. For thicker films, the lamellar orientation shows a transition from parallel stacking near the substrate to homeotropic standing in the air surface. The fundamental understanding of this self-oriented LC diblock copolymer thin film behaviors will be important for further nano-patterning or electrical/optical applications.

#### **D9.31**

**CONTROLLED PATTERN GEOMETRY AND SPACING OF AMPHIPHILIC DIBLOCK COPOLYMER AGGREGATES BY LANGMUIR-BLODGETT DEPOSITION.** Caitlin Devereaux and Shenda M. Baker, Department of Chemistry, Harvey Mudd College, Claremont, CA.

Nanometer-size aggregates of amphiphilic diblock copolymers of poly(styrene) and poly(ethylene oxide) (PS-PEO) can be prepared at the air-water interface and deposited on a hydrophilic substrate by the Langmuir-Blodgett (LB) technique; the geometry of the resultant aggregates depends on the block asymmetry and the spreading solution concentration. Diblock copolymers with greater than 15% PEO by weight form separated dot aggregates, surface micelles, as determined by examination of the resultant film by atomic force microscopy. The spacing of the dots can be controlled by choosing the appropriate region on the two-dimensional surface pressure vs area isotherm for the LB deposition. For diblocks with less than 15% by weight PEO, spaghetti and conglomerate structures can be selectively prepared. Selection of aggregate type is dictated by the factors of diblock asymmetry and spreading solution concentration, but does not depend on deposition pressure or speed. As expected, only the spacing between features is influenced by deposition pressure. The aggregates thus formed are relatively stable. Furthermore, although PS is glassy at room temperature, these features show remarkable flexibility upon compression due to the excessively thin dimensions.

#### **D9.32**

**PEPTIDE RECOGNITION AND NUCLEATION OF SEMICONDUCTOR AND MAGNETIC MATERIALS.** Sandra R. Whaley, Christine Flynn, Erin Gooch, Jamie Schaeffer, and Angela M. Belcher, University of Texas at Austin, Dept of Chemistry and Biochemistry, Austin, TX.

A peptide combinatorial approach has been used to select proteins that bind to non-traditional inorganic substrates, such as semiconductors and magnetic materials, for the purpose of nucleating these materials on the nanoscale and producing semiconductor-magnetic heterostructures. The peptides are displayed on the surface of a bacteriophage, a virus which infects bacteria. Those clones which bind to the surface of interest are sequenced and mapped, allowing for analysis of the chemical driving forces of these interactions. Positive binding peptides were characterized for substrate recognition, discrimination, and binding using X-ray Photoelectron Spectroscopy (XPS), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Fluorescence Microscopy, and Atomic Force Microscopy (AFM). In addition, specific clones have been isolated which can nucleate ZnS nanocrystals from an aqueous solution. The development of bifunctional systems in order to organize semiconductor-magnetic heterostructures will be discussed.

#### **D9.33**

**IN-PLANE COBALT NANOARRAY BY ELECTRODEPOSITION IN HIGHLY ORDERED NANOPOROUS ALUMINUM OXIDE FILMS.** Ming Sun, Giovanni Zangari, Mohammed Shamsuzzoha, and Robert M. Metzger, Center for Materials for Information Technology, The University of Alabama, Tuscaloosa, AL.

Nano-scale arrays of ferromagnetic particles (patterned media) are potential media for ultra-high density magnetic recording. For instance, we recently fabricated hexagonally ordered porous alumina structures (alumite) with ordered areas of up to 100 square micrometers [1]. Using such templates, we produced highly ordered ferromagnetic in-plane magnetic anisotropy Co arrays by electrodeposition (from a 0.1 M CoSO<sub>4</sub> solution) into the pores of ordered alumite (pore to pore distance 80-160 nm) using two different voltage waveforms. The magnetic properties were studied as a

function of nano-particle size (diameter 20-60 nm, length 5-100 nm). Using conventional AC sine-wave voltage waveforms at 200 Hz, the electrodeposited Co array grows with the crystallographic c-axis in the plane of the film, with a (1,0,-1,0) orientation [1]. However, the wide distribution of particle lengths [1] could explain the lack of any transition to in-plane magnetic anisotropy at low average thickness. In contrast, Co electrodeposition using an asymmetric rectangular voltage waveform (500 Hz) yielded a uniform particle length, because of an increased Co nanocrystal nucleation rate. In this case, a transition from perpendicular to in-plane anisotropy was observed with decreasing average thickness. Annealing this sample showed further improved magnetic properties. This close control of nucleation and growth enables the production of thin Co arrays with in-plane anisotropy. To further characterize these arrays, the magnetic viscosity and fluctuation field of the Co arrays has been measured as function of particle diameter and length, and compared to previous results obtained on thick Fe arrays in alumite [2]. This work was supported by the US Army Research Office (Grant DAA-H04-96-1-0316). [1] R.M. Metzger, V.V. Konovalov, M. Sun, T. Xu, G. Zangari, B. Xu, M. Benakli, & W.D. Doyle; IEEE Trans. Magn. 36: 30 (2000). [2] F. Li, R.M. Metzger, & W.D. Doyle; IEEE Trans. Magn. 33: 3715 (1997).

#### **D9.34**

**SELF-ORGANIZED MESOSCOPIC PATTERNING IN POLYMER SOLUTIONS.** V. Samuilov, Y-S. Seo, M. Rafailovich, J. Sokolov, Materials Science Department, SUNY-Stony Brook, NY; V. Ksenevich, Johann Wolfgang Goethe-University, Frankfurt/Main, GERMANY; I. Bashmakov, L. Solovjova, State University of Belarus, Minsk, BELARUS.

A novel and simple approach of non-lithographic fabrication of two dimensional mesoscopic networks with the feature size down to 50 nm has been developed. The technique is based on the self-organized patterning in a thin layer of complex liquid (diluted nitrocellulose solution) in the presence of humid atmosphere. The sub-micron sized water droplets are trapped at the surface and form compact regular aggregates. The polymer was found to be precipitated at the water-polymer solution interface, forming a layer encapsulating the droplets and preventing their coalescence. Two dimensional mesoscopic honeycomb carbon structures were produced by high temperature annealing of the nitrocellulose precursors. The structured polymer networks were also utilized as masks for the further reactive ion etching of surfaces of initial epi-layer of GaAs and GaAs/AlGaAs delta-doped heterostructures [1]. This technique can find applications for low dimensional mesoscopic devices. The support of the NSF - MRSEC Program and The Foundation of Basic Research of Belarus is kindly acknowledged. [1] V.A. Samuilov et al., Superlattices and Microstructures, 25 (1999) 127.

#### **D9.35**

**AN FIB MICRO-SAMPLING TECHNIQUE FOR SITE-SPECIFIC MATERIALS CHARACTERIZATION.** Toshie Yaguchi, Ryoichi Urao, Ibaraki Univ., School of Engineering, Ibaraki, JAPAN; Takeo Kamino, Hitachi Science Systems, Ltd., Ibaraki, JAPAN; Tsuyoshi Ohnishi, Takahito Hashimoto, Hitachi Ltd., Instruments Division, Ibaraki, JAPAN; Kaoru Umemura, Satoshi Tomimatsu, Hitachi Ltd., Central Research Laboratory, Tokyo, JAPAN.

Recently we developed a new FIB micro-sampling technique for electron transparent thin foil preparation. In this method, a bulk specimen remains intact during extraction of a micro-sample, and both cross sectional and plan view thin foil preparations are possible. The micro-sample is extracted from the bulk specimen using a micro-manipulator, and it is transferred to an edge of a carrier to produce an electron transparent thin foil. Extraction and mounting of the micro-sample on the carrier are carried out in the FIB instrument. Since a micro-sample is mounted on the specimen-carrier, and the materials for the carrier can be chosen by the operator, the geometry of the original specimen is not a limiting factor for energy dispersive X-ray (EDX) analysis. In failure analysis of semiconductor devices, it is difficult to localize a site to be characterized using the FIB technique, because the very small site cannot be observed either by SIM (Scanning Ion Microscope) image or SEM (Scanning Electron Microscope) image available with the FIB system. We have developed a site specific thin foil preparation method using a combination of FIB micro-sampling technique and microscope equipped with both SEM (Scanning Electron Microscope) and STEM (Scanning Transmission Electron Microscope) detectors. In this method, the specimen is mounted on an FIB-STEM compatible specimen holder, so that the specific site can be located in the FIB and STEM using the same holder. SEM images may be used to observe surface structures of the milling area, and the STEM images may be used to observe structures inside of the milled surface. Thus, milling of a specimen by FIB, and observation of the milled surface by SEM and STEM at an intermediate voltage are alternately carried out until an electron transparent thin foil specimen from the site is obtained. The advantage of this method over conventional FIB milling techniques is

that thin foil preparation can be performed with a good positional accuracy of better than 100nm. The instruments used in this study were the Hitachi FB-2000A FIB system and Hitachi HD-2000 cold field emission 200kV analytical STEM. The method was applied to the characterization of semiconductors.

#### **D9.36**

Abstract Withdrawn.

#### **D9.37**

**FABRICATION OF HELICALLY PERFORATED FILMS.**

**Kenneth D. Harris**, Michael J. Brett, University of Alberta, Department of Electrical and Computer Engineering, Edmonton, CANADA.

We will present a simple method for the fabrication of thin films or membranes perforated by helically shaped holes. Using electron beam evaporation at highly oblique deposition angles, in conjunction with computer controlled substrate rotation, highly porous (40-50% of bulk density) thin films of helically microstructured SiO<sub>2</sub> were deposited. Typical helix dimensions are on the order of 2µm in total thickness, and comprise from 1 to 20 turns. This technique, often called glancing angle deposition (GLAD), is also capable of producing other microstructures, such as vertical and slanted posts, and chevron structures. Helical films produced by this technique were filled with photoresist and, subsequently, etched to remove the helices. A continuous photoresist cast of the original film remained. It has been found possible to produce these perforated photoresist films from helices distributed either randomly over the substrate, or from structures grown on a well defined, periodic array. Use of other membrane materials and potential applications in the fields of optics and microfluidics will be discussed.

#### **D9.38**

**SURFACE POTENTIALS OF CONJUGATED MOLECULES ON METAL SURFACES: MEASUREMENTS USING ELECTROSTATIC FORCE MICROSCOPY AND CALCULATIONS USING PHYSICALLY-BASED MODELS.** Stephen W. Howell, Purdue Univ., Dept. of Physics, W. Lafayette, IN; Helen A. McNally, David B. Janes, Ferdows Zahid, Supriyo Datta, Purdue Univ., School of Elect. and Computer Engineering, W. Lafayette, IN; Scott Crittenden and Ronald Reifenberger, Purdue Univ., Dept. of Physics, W. Lafayette, IN.

Key issues in determining the conducting properties of organic molecules between metal electrodes include determining the relative potential of the molecule with respect to the metal electrode and the relative position of the Fermi level with respect to the molecular states [1]. This information is comparable to the information required to predict band line-ups in semiconductor heterostructures or metal-semiconductor (Schottky) junctions. Prior experiments have addressed the surface potential, i.e. the modification of the work function, of Au surfaces coated with series of molecules [1-3]. These studies have focussed on the changes of surface potential with chain length and/or top end group. To date, a detailed physical picture of the absolute value of the observed surface potential has not emerged. In the present study, we are measuring the surface potential of molecules of interest for molecular electronics applications and integrating these results with ab initio calculations of the electronic levels and conduction properties of molecular layers on metal surfaces. The experimental study was conducted using an electrostatic force microscope [5]. This technique, based on standard scanning force microscopy technology, allows the surface potential to be probed with a high lateral resolution. A heavily doped silicon atomic force microscope (AFM) tip was used to determine the surface potentials above various organic monolayers on flat Au surfaces. In the standard electrostatic potential measurement, the surface potential of the sample was determined by varying the voltage on the tip until the electrostatic component of the force was eliminated. Extensions of the technique can provide information on charge transfer between the metal surface and the molecule. Samples studied to date include self-assembled monolayers of alkyl-thiol molecules, conducting dithiol molecules such as xylyl dithiol, and organic molecules with charge-transfer complexes, as well as biological molecules. The surface potential measurements can be correlated with observed current-voltage behavior [1] and can be used to verify the parameters needed in ab initio calculations of the current-voltage characteristics of metal/molecule/metal systems. The comparison of the measured data and theoretical predictions can provide a useful means to evaluate and interpret molecular conduction results [1]. [1] W. Tian, S. Datta, S. Hong, R. Reifenberger, J.I. Henderson and C.P. Kubiak, *J. Chem. Phys.* 109, 2874 (1998). [2] S.D. Evans and A. Ulman, *Chem. Phys. Lett.* 170, 462 (1990). [3] J. Lu, et al., *Langmuir* 15, 8184 (1999). [4] R.W. Zehner, et al., *Langmuir* 15, 1121 (1999). [5] M. Nonnenmacher, et al. *Appl. Phys. Lett.* 58, 2921 (1991).

#### **D9.39**

**MOLDING POLYMERS AT THE NANOSCALE TO PRODUCE PATTERNED FEATURES OF SELF-ASSEMBLED MONOLAYERS (SAMS).** Jianling Li, Mei-wei Tzao, John F. Rabolt, Univ. of Delaware, Dept. of Materials Science and Engineering, DE.

Microcontact and nanocontact printing has been used to produce patterned self-assembled monolayers (SAMs) on a variety of substrates such as gold, silver, or glass. In this technique, an elastomeric stamp, fabricated from poly(dimethylsiloxane) (PDMS) is wetted with a molecular, polymeric, or liquid "ink". The molecules are then transferred by conformal contact to a substrate. This paper presents different patterned features of SAMs on gold surfaces that were generated using this procedure. Features of patterned SAMs using Solutions of alkanethiols with dimensions as small as one micrometer or less were produced. The capability of patterning a surface with different monolayers allows us to easily tailor the physical and/or chemical properties of the surface. Atomic force microscopy (AFM) studies of these SAMs revealed a dependence on the formulation of siloxane polymers, the aspect ratios of the features, and the concentration of the thiol solutions. The patterned SAMs can be used as components in electrical and optical devices, as resists for further processing and as substrates for enhanced cell growth.

#### **D9.40**

**THE CONDUCTION CHARACTERISTICS AND SURFACE ELECTRONIC PROPERTIES OF A LOW-RESISTANCE, OHMIC METAL/MOLECULE/SEMICONDUCTOR NANOCONTACT.** Nien-Po Chen, Stephen W. Howell, Takhee Lee, Ronald Reifenberger, Purdue Univ., Dept. of Physics, W. Lafayette, IN; Marcus Batistuta, David B. Janes, Michael R. Melloch, Purdue Univ., School of Elect. and Computer Engineering, W. Lafayette, IN; Jia Liu, Ronald Andres, Purdue Univ., School of Chemical Engineering, W. Lafayette, IN.

In order to realize nanoscale structures such as low-resistance contacts, it is necessary to employ processes that can provide i nanoscale features as well as well-controlled surfaces and interfaces at the nanometer scale. Through appropriate choices of semiconductor surface layers and the metals (or molecules) used to interface with the surface, it is possible to achieve these goals in ex-situ processing. A large-area example of an ex-situ structure with well-controlled interfaces is provided by a nonalloyed ohmic contact to n:GaAs employing a surface layer of low-temperature-grown GaAs (LTG:GaAs) with specific contact resistances as low as  $3 \times 10^{-7} \Omega\text{-cm}^2$  [1]. A quantitative conduction model of this contact structure indicates that activated donor densities well above the bulk amphoteric limit have been achieved near the surface and that the surface Fermi level is not pinned at midgap [2]. We have previously reported a self-assembled, low-resistance ohmic nanocontact consisting of a 4 nm diameter Au nanocluster tethered to a LTG:GaAs/n:GaAs surface by a monolayer of a conjugated organic molecule (xylyl dithiol) [3]. This presentation will describe a quantitative conduction model for this nanometer scale ohmic contact, which can be described by a metal/"insulator"/semiconductor structure. The "insulator" (xylyl dithiol) is relatively conductive and does not appear to be a limiting factor in the overall conductivity. The model indicates that tunneling is the dominant conduction mechanism, with the midgap states in the LTG:GaAs surface layer playing a significant role. Fitting to the measured contact resistance values indicates that the surface barrier in this structure ( $< 0.5$  eV) is below that expected for midgap Fermi level pinning (0.7 eV). In order to verify this observation, we have characterized the surface potential of the LTG:GaAs at various stages in the processing using electrostatic force microscopy [4]. This technique allows direct observation of the time evolution (over hours) of the surface potential following the stripping of the surface oxide. Finally, we will describe the semiconductor engineering and surface chemistry that allows ex-situ interfaces with well-controlled electrical properties. [1] M. Patkar, et al., *Appl. Phys. Lett.* 66, pp. 1412 (1995). [2] Nien-Po Chen, et al., *J. Appl. Phys.*, 88, 309 (2000). [3] Takhee Lee, et al., *Appl. Phys. Lett.*, 76, 212 (2000). [4] M. Nonnenmacher, et al., *Appl. Phys. Lett.* 58, 2921 (1991).

#### **D9.41**

**AN EFFICIENT ROUTE FOR SILANE-COATED MAGNETIC NANOPARTICLES.** Kurikka V.P.M. Shafi, Abraham Ulman, Polytechnic University, Department of Chemical Engineering and Chemistry, Brooklyn, NY; Xingzhong Yan, Nan-Loh Yang, CUNY at Staten Island, Department of Chemistry, Staten Island, NY; The NSF MRSEC for Polymers at Engineered Interfaces.

Sonochemistry is a fast and efficient technique for coating of octadecyltrihydrosilanes (CH<sub>3</sub>(CH<sub>2</sub>)<sub>17</sub>SiH<sub>3</sub>) on γ-Fe<sub>2</sub>O<sub>3</sub> nanoparticle surfaces. Infrared spectroscopy, as well as thermal analysis confirm that complete coating is achieved after 1 h. We present EPR, as well as magnetic studies of the coated nanoparticles.

**D9.42**

Abstract Withdrawn.

**D9.43**

**FABRICATION OF PHOTONIC CRYSTALS USING METAL CLUSTERS AS NUCLEI FOR SELF-FORMATION OF ETCHING MASKS.** Tetsuya Tada, Toshihiko Kanayama, Joint Research Center for Atom Technology (JRCAT), National Institute for Advanced Interdisciplinary Research, Tsukuba, JAPAN; Vladimir V. Poborchii, JRCAT-Angstrom Technology Partnership (ATP), Tsukuba, JAPAN.

We have fabricated 2D photonic crystals (PC's) with photonic band gaps of visible light range by periodically arranging Si nanopillars. The fabrication process uses Fe clusters as nuclei for self-formation of etching masks to obtain high-aspect-ratio Si nanopillars. Arrays of Fe clusters were formed on Si substrates by electron beam lithography lift-off processes followed by vacuum evaporation of Fe to a nominal thickness of 1-2 nm. The substrates were ECR etched at -135°C with SF<sub>6</sub>. During the etching, reaction products in the plasma, S<sub>x</sub>F<sub>y</sub>, condensed around the clusters, leading to the self-formation of uniform size etching masks. The catalytic property of Fe clusters resulted in durable mask formation, enabling us to fabricate Si nanopillars with diameters of 10-150 nm and height of 0.2-3 μm. Reflection spectra of the fabricated PC's were measured, and compared with theoretical calculations of the photonic band structures. The PC's exhibited reflection peaks depending on the lattice structure and polarizations; e.g. for 270 nm period, the reflection peak was around 500-600 nm, which is consistent with the theoretical calculation[1,2]. This demonstrates that the above fabrication process has sufficient accuracy to yield PC's with visible band gaps. We also fabricated waveguide structures using PC's with line defects. Their properties will be discussed. [1] V.V. Poborchii, T. Tada, and T. Kanayama; Appl. Phys. Lett. 75 (1999) 3276. [2] T. Tada, V.V. Poborchii, and T. Kanayama; Jpn. J. Appl. Phys. 38 (1999) 7253.

**D9.44**

**MICROSENSORS THAT FUNCTION ON THE BASIS OF SURFACE TENSION AND WETTABILITY.** Phillip Wapner, Wesley Hoffman, Air Force Research Laboratory, Edwards Air Force Base, CA.

The displacement of non-wetting fluid droplets contained within capillaries that have axial profiles that are non-uniform can be used to accurately and reproducibly measure the forces acting upon these droplets. The position of droplets within such micro-sensors is dictated by surface tension, wettability, geometric configuration of the confining walls, and the forces acting upon the droplet. These micro-sensors can measure pressure and acceleration, and can also be made to operate as micro-valves, micro-switches, optical shutters, as well as other devices. They have no moving mechanical parts to wear out, and can theoretically endure high amounts of over-actuation and still return to initial levels of accuracy and precision without harm. The axial profiles of these shaped capillaries are easily fabricated using microtube technology developed at the Air Force Research Laboratory at Edwards Air Force Base. However, it is also possible to use non-circular shaped voids and still achieve similar capabilities with some limitations. These non-circular shaped voids can be manufactured using more conventional MEMS technologies such as photolithography and LIGA.

**D9.45**

**SONOCHEMICAL PREPARATION OF MAGNETIC NANOPARTICLES.** Kurikka V.P.M. Shafi, Abraham Ulman, Polytechnic University, Department of Chemical Engineering and Chemistry, Brooklyn, NY; Xingzhong Yan, Nan-Loh Yang, CUNY at Staten Island, Department of Chemistry, Staten Island, NY; Henry White, Miriam Rafailovich, Jonathan Sokolov, State University of New York at Stony Brook, Department of MS&E, Stony Brook, NY; The NSF MRSEC for Polymers at Engineered Interfaces.

The in-situ preparation of stable Fe<sub>2</sub>O<sub>3</sub> colloids was carried out by sonicating Fe(CO)<sub>5</sub> and different surfactants in hydrocarbon solvents. The magnetic properties of the amorphous nanoparticles depend on the nature of the surfactant coating. The stability of the colloids depends on the nature of the solvent.

**D9.46**

**CONTROLLING INTER-PARTICLE INTERACTIONS BY NANO-SCALE ENGINEERING.** Geoffrey F. Strouse, Robert W. Meulenberg, University of California-Santa Barbara, Dept of Chemistry, Santa Barbara, CA.

Three-dimensional arrays of nanomaterials for nano-electronic applications can be designed by control of the electrostatic packing, the van der Waal interactions, and the inter-chain interactions. The simplest method of assembly is to apply ligand templating, either through biological or organic spacers, to form 3-D constructs. A

second level of design can be incorporated by choice of the surface passivant. We demonstrate non-lithographic assembly strategies for formation of 3-D assemblies of q-CdSe and nano-scale Au. The surface passivant allows controlled inter-particle interactions, which can be tuned by manipulation of the surface structure. High pressure and temperatures can tune the activation barrier for structural transitions in these materials. Correlated analysis of ATR-FTIR, FT-Raman, XRD, DSC, and photoluminescence measurements as well as characterization by electronic absorption, TEM, and TGA will be presented.

**D9.47**

**SELF-ASSEMBLY AND OPTICAL PROPERTIES OF GOLD@SILICA SUPERPARTICLES.** Steven L. Tripp, Bryce Sadtler, Jun Xu, Alexander Wei, Purdue University, Department of Chemistry, West Lafayette, IN.

Spherical arrays of 20-80 nm colloidal gold particles were formed around a central silica core in aqueous solutions. Electrostatic and cohesive interactions were modulated systematically by surface functionalization. Thiol-terminated oligo(ethylene glycol) chains and aminotrialkoxysilanes were found to be appropriate surfactants for modulating the surface properties of the gold and silica colloids, respectively. Colloidal charge densities were measured as a function of surfactant and pH by zeta potential analysis. Hetero-assembly was accomplished simply by mixing stoichiometric amounts of gold and silica colloid; the resulting superparticle ensembles were limited in solubility but easily redispersed. Characterization by transmission electron microscopy, optical absorption spectroscopy, and near infrared surface-enhanced Raman scattering (NIR-SERS) will be discussed in the context of their potential as Raman-based sensors.

**D9.48**

Abstract Withdrawn.

**D9.49**

**SUB-MICRON PATTERNED ANODIC OXIDATION OF ALUMINUM THIN FILMS.** Qiyu Huang, Whye-Kei Lye, Michael L. Reed, University of Virginia, Department of Electrical Engineering, Charlottesville, VA.

Alumina formed by the electrochemical anodization of bulk aluminum is known to have a porous structure. Sub-100 nanometer pores with aspect ratios as high as 1000:1 can easily be formed without elaborate processing. Anodization of aluminum thus provides the basis for the inexpensive, high throughput microfabrication of structures with near vertical sidewalls. In this work we explore the patterned anodic oxidation of deposited aluminum thin films, facilitating the integration of this technique with established microfabrication tools. An anodization barrier comprising a layer of Polymethylmethacrylate (PMMA) is deposited onto 300 nm thick aluminum films. The barrier is subsequently patterned and the exposed aluminum anodized in a 10% sulphuric acid solution. Barrier patterning techniques utilized in this study include optical, ion-beam and nano-imprint lithography. Sharp edge definition on micron scale patterns have been achieved optically. Extension of this technique to smaller dimensions by ion-beam and nano-imprint lithography is presented. We further report on the observation of contrast reversal of anodization with very thin PMMA barriers, which provides a novel means of pattern transfer. Potential applications and challenges will be discussed.

**D9.50**

**ELECTRICAL TRANSPORT IN LOW DIMENSIONAL MESOSCOPIC NETWORKS.** V. Samuilov, M. Rafailovich, J. Sokolov, Dept of Materials Science, SUNYSB, NY; V.K. Ksenevich, Johann Wolfgang Goethe-University, Frankfurt-Main, GERMANY; J. Galibert, Laboratoire de Physique de la Matière Condensée, SNCMP-INSA, Toulouse, FRANCE.

The self-organized patterning in a thin layer of complex liquid (diluted nitrocellulose solution) was used to produce low dimensional mesoscopic polymer networks [1]. Two dimensional mesoscopic honeycomb - shape carbon structures were manufactured by high temperature annealing of the nitrocellulose precursor. The networks were also used as non-lithographic mask on a semiconductor surface in order to decrease a dimension of 2-D electron gas in the initial GaAs/AlGaAs delta-doped heterostructures. The electrical transport properties of the obtained structures were studied in a temperature range from 1.9 to 300 K and in pulsed magnetic fields up to 35 T. A Crossover from Mott variable range hopping to the Colom-b-gap Efros-Shklovskii variable range hopping has been observed experimentally in mesoscopic carbon structures. From the magnetoresistance vs magnetic field curves three regions were defined of low, intermediate and high magnetic field. At low fields, ln(R/R<sub>0</sub>) is proportional to B<sup>2</sup>. In the intermediate range, the magnetoresistance is linear on B. The dependence of magnetoresistance on B in the high field region is much weaker (sub-linear) and reaches saturation at the

highest fields and lowest temperatures. At high temperatures, where the hopping distance is comparable to the localization length, the observed small negative magnetoresistance in our samples is consistent to the weak-localization picture. Magnetoresistance of patterned GaAs/AlGaAs delta-doped is negative. In magnetic fields higher than about  $B=5T$  the magnetoresistance is positive and saturates at  $B>12T$ . At  $B=0$ , the resistance presents typical behavior of a two-dimensional insulator. Below about 20 K, the data follows the Mott variable-range-hopping mechanism for two dimensions. Low conductivity of the sample with the network could be explained by the model of isolated "metal lakes" coupled by weak tunneling junctions in the framework of the 2-D network. The support of the NSF - MRSEC Program and The Foundation of Basic Research of Belarus is kindly acknowledged. [1] V.A. Samuilov et al., Superlattices and Microstructures, 25 (1999) 127.

**D9.51**  
CHROMIUM OXIDE NANOPARTICLES FABRICATED BY A UNIQUE TECHNIQUE: LASER-INDUCED SOLUTION DEPOSITION. Zhenchen Zhong, Institute for Micromanufacturing, Louisiana Tech University, Ruston, LA; Department of Physics, Grambling State University, Grambling, LA.

We have demonstrated that well-dispersed nanoscale chromium oxide particles can be fabricated by laser-induced solution deposition (LISD) from the solution of  $CrCl_2$  solute dissolved in organic solvents containing THF and cyclohexane. The particles are uniform in composition and contain little contamination. The distribution of the particles is narrow in three sizes: 230 nm, 350 nm and 400 nm. We have discussed the kinetics of forming these three kinds of nanoparticles and the difficulty in obtaining single-phase chromium oxide. We have successfully shown that LISD is a unique technique for fabricating nanoscale chromium oxide particles with uniform composition and controllable size with narrow particle distribution.

**D9.52**  
SPATIALLY CONTROLLED CdSe NANOCRYSTAL DISTRIBUTION IN PHASE SEPARATED POLYMER BLEND FILMS. Harumi Asami, Souichirou Saita, Itaru Kamiya, Kenichi Yoshie, Yokohama Research Center, Mitsubishi Chemical Corporation, Yokohama, JAPAN.

Semiconductor nanocrystals (NCs), also known as colloidal quantum dots, are small molecular clusters which size is ca. 1 to 10 nm in diameter. Their unique optoelectronic properties arising from 3-dimensional confinement of carriers have attracted much attention both from the scientific and the technological points of view. These nanocrystals can be incorporated into a matrix such as polymers, to form thin films that consist of nanocrystal-polymer composites. Such organic/inorganic hybrid structures hold great promise for their applications, for example, to electroluminescent devices, photovoltaic cells or nonlinear optical devices. However, in order to meet stringent requirements for realizing such sophisticated devices with high quantum efficiency, it is imperative that we have good control over their structures. In an attempt to achieve such goal, we have performed investigation on the surface morphology of NC-polymer composite thin films containing tri-*n*-octylphosphine oxide (TOPO)-capped CdSe NCs. We studied the morphology and the distribution of CdSe NCs in CdSe/Polystyrene (PS), CdSe/Polymethylmethacrylate (PMMA), and CdSe/PS/PMMA composite thin films fabricated by spin coating using combined optical microscopy and photoluminescence (PL) imaging, and find that they are significantly different. The structures are formed on glass substrates via demixing of CdSe nanocrystals and polymers during spin coating. Comparing CdSe/PS and CdSe/PMMA, large aggregation of CdSe NCs are found to form in PMMA matrix. In the CdSe/PS/PMMA film, the polymer blend phase separate, and the NCs are found to segregate preferentially to the PS matrix. Gaining detailed information about such NC-polymer interactions will allow us to prepare complex structures for optoelectronic devices.

**D9.53**  
DYNAMIC LIGHT SCATTERING AND OPTICAL SPECTROSCOPY AT CdSe NANOCRYSTALS AND CLUSTERS. Andreas Eichhoefer, Carsten von Haenisch, Dieter Fenske, Forschungszentrum Karlsruhe, Institut fuer Nanotechnologie, Karlsruhe, GERMANY; Uri Banin, The Hebrew University, Givat Ram, Department of Physical Chemistry, Jerusalem, ISRAEL.

High performance dynamic light scattering has been used to determine the hydrodynamic radius of CdSe nanocrystals and CdSe cluster molecules in a size range of 1 to 10 nm in different solvents. From these measurements it was possible to obtain the radius including the ligand shell of these particles under the same conditions usually used for optical spectroscopy. This has advantages compared to the well established methods TEM and powder x-ray diffraction (using scherrer equation). TEM only determines the particle radius

without the organic shell at high temperatures and powder x-ray diffraction doesn't work very well in the size range smaller than 3 nm. For the CdSe cluster molecules, which have also been characterised by single crystal x-ray diffraction, it was possible to compare the radius in solution with the molecular structure in the solid. These CdSe cluster molecules were prepared using the organometallic reaction of  $CdCl_2$  with the silylated chalcogenide compounds  $Ph-Se-SiMe_3$  and  $Se(SiMe_3)_2$  in the presence of tertiary phosphine ligands. The cluster compounds were then crystallised. The particle radii in solution will be discussed and compared with radii obtained by other methods such as TEM, powder x-ray diffraction or single crystal x-ray diffraction. Also presented are the synthesis and structures of the CdSe cluster molecules as well as optical spectra of these clusters and the CdSe nanocrystals.

**D9.54**  
FUNCTIONAL NANOMATERIALS ASSEMBLY THROUGH BIOMIMETICS. Mehmet Sarikaya, Daniel Heidel and Richard Humbert, MS&E, University of Washington, Seattle, WA; Stanley Brown, Molecular Cell Biology, University of Copenhagen, Copenhagen, DENMARK.

Many multicellular organisms produce hard tissues such as bones, teeth, shells, skeletal units, and spicules that incorporate both structural macromolecules (lipids, proteins, and polysaccharides) and minerals of, perhaps, 60 different kinds including hydroxyapatite, calcium carbonate, magnetite, and silica. The structures of biocomposites are highly controlled from the nanometer to the macroscopic levels, resulting in complex, hierarchical architectures that provide multifunctional properties (mechanical, optical, magnetic) that usually surpass those of analogous synthetically manufactured materials with similar phase compositions. Biological materials are assembled in aqueous environments under mild conditions using biomacromolecules which have specific interactions with the mineral phase. Combinatorial genetic techniques permit isolation of specific recognition elements for surfaces, including those not recognized by natural proteins, in the absence of a priori prediction of necessary structures. Here we demonstrate controlled assembly of nanometer-scale gold particles on functionalized spherical and flat surfaces (resembling quantum dot structures) in aqueous solutions using engineered gold-binding proteins as recognition elements. Furthermore, using a newly-developed genetic system in the bacterium *E. coli* we show a control of crystal growth via protein-mediation. The results could have significant implications in tailoring formation and assembly of genetically-controlled ordered structures for applications in nano- and molecular technologies.

**D9.55**  
A POTENTIAL INTERCONNECTION METHOD IN MOLECULAR ELECTRONICS. Meng Tao, Louisiana Tech Univ, Inst for Micromanufacturing and Dept of Electrical Engineering, Ruston, LA.

To bring molecular electronics to life, the research has to address three major issues: finding or developing molecules which possess logic/memory functions to serve as 'devices', developing an interconnection technology to connect these molecules into circuits, and developing circuit architectures which best utilize the advantages provided by molecular electronics. Most of the current research focuses on the device side, and significant progress is being made in finding and understanding molecular devices. Here we propose a method to electrically connect molecular devices, which has the potential to develop into an interconnection technology for 3-dimensional molecular electronic circuits. The method is based on electric-bias-induced polarization and electric-pulse-induced chemical reactions. Two molecules to be connected are oppositely biased to induce opposite charges in them. The opposite charges will create electrostatic attraction which pulls the two molecules together. Then an electric pulse is applied across the two molecules to trigger a chemical linking reaction between them. The electric pulse overcomes the activation energy for such a reaction. Chemical linking reactions to produce conjugated resultant molecules are proposed for several hydrocarbon molecules, such as poly(phenylene) and poly(acetylene) molecules, with various end groups, such as vinyl, phenyl, and acetyl groups. Applications of this method in assembling 3-terminal molecular devices and 3-dimensional molecular electronic circuits are speculated. Major challenges in realizing this interconnection method are also outlined.

**D9.56**  
THE PREPARATION AND OPTICAL PROPERTIES OF Au-SHELL SUBMICRON PARTICLES. Tianhao Ji, Yair Avny, Dan Davidov, Hebrew Univ of Jerusalem, Racah Institute of Physics and Dept of Organic Chemistry, Jerusalem, ISRAEL.

There is much interest in gold nanoparticles for nanotechnological applications. Recently, tunable surface plasmon resonance has been demonstrated for gold nanoparticles on silica nanoparticles as a

function of coverage. Here we report on the successful fabrication and optical studies of Au nanoshells on uniform polystyrene (PS) latex beads (mostly with diameter of 800 nm). We have combined self-assembly and seeding methods. The 3 nm Au nanoparticles in aqueous media were first assembled onto the surface of PS particles and then grown into metal nanoshells by seeding method. The thickness of the Au-shell can be controlled efficiently by changing the concentration of  $\text{HauCl}_4$  and  $\text{NH}_2\text{OH}$  in the solution. The metal nanoshells obtained were characterized by UV-vis absorption spectroscopy and transmission electron microscopy (TEM). The TEM measurements demonstrate that the bonded gold nanoparticles on the surface of PS form either single particles or clusters but can be converted into the gold nanoshells (complete or almost complete) with 10-20 nm thickness after treatment. The Absorption spectroscopy of the Au-coated PS submicro-particles shows that the optical extinction spectrum consists of two maxima due to scattering of the Au-coated particles and surface plasmon resonance of the Au-shell, respectively. The former can be interpreted by Rayleigh-Gans theory and the latter by Mie's theory. The position of the plasmon peak depends upon the thickness of the Gold nanoshell. The advantage of PS when compared to silica nanoparticles is the ability to prepare hollow nanoshells of composite materials containing Au. We hope to report also on magnetic PS covered with Au nanoshells. Such functionalized nanoparticles can be used in optical device, photonic band gap and biosensors. This work was supported by AFIRST and the VW foundation.

SESSION D10: ELECTRONIC AND MAGNETIC PROPERTIES OF NANOSTRUCTURES

Chair: John A. Rogers  
Friday Morning, December 1, 2000  
Constitution B (Sheraton)

**8:30 AM D10.1**

**ELECTRICAL CONDUCTION THROUGH ORDERED MONO-LAYER AND BILAYER ARRAYS OF Au NANOPARTICLES LINKED BY ORGANIC MOLECULES.** Jia Liu, School of Chemical Engineering, Purdue University, West Lafayette, IN; Marcus Batistuta, David Janes, School of Electrical and Computer Engineering, Purdue University, West Lafayette, IN; Ronald P. Andres, School of Chemical Engineering, Purdue University, West Lafayette, IN.

Well-ordered monolayer and bilayer arrays of Au nanoparticles that are encapsulated by dodecanethiol molecules are selectively self-assembled on an oxidized Si substrate on which interdigitated Au electrodes have been pre-deposited. Electron transport between the electrodes due to lateral conduction through the nanoparticle film is measured. By displacing the dodecanethiol molecules surrounding the Au nanoparticles with selected aryl dithiols and porphyrins, the electrical conductance of the film is enhanced. The conductance can also be modified by absorption of foreign molecules and this phenomenon can serve as the basis of a chem-resistive sensor.

**8:45 AM D10.2**

**ELECTRONIC COUPLING IN ORGANICALLY BRIDGED METAL NANOPARTICLES.** James P. Novak, Lisa B. Lowe, A. Blaine House, Louis C. Brousseau, III, Dan L. Feldheim, North Carolina State University, Dept. of Chemistry, Raleigh, NC.

Nanoscale metal particles have the potential to be used as building blocks for nanoscale electronic devices. However, integrated devices require a fundamental understanding of the electronic communication between individual components. To explore these fundamental interactions we must investigate particles with fixed interparticle distance, symmetry and aggregation numbers. We have synthesized symmetry controlled metal nanoparticle arrays using rigid phenyl-acetylene bridging ligands. Investigations of the electronic and electromagnetic coupling between particles in these arrays will be discussed.

**9:00 AM \*D10.3**

**QUANTUM COHERENCE IN SUB-10NM METAL WIRES.** Douglas Natelson, Robert L. Willett, Kenneth W. West, Loren N. Pfeiffer, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

We report weak localization studies of quantum coherence in metal nanowires with widths as small as 5 nm, demonstrating that structures fabricated at sub-50 nm length scales can reveal coherence phenomena not accessible in larger devices. Through selective etching of cleaved MBE-grown substrates, we produce precise nanoscale surface relief then used as a stencil for metal deposition. This nonlithographic method of lateral definition allows the fabrication of metal (AuPd) nanowires greater than one micron in length with widths below 5 nm, a previously unexplored size regime in studies of quantum corrections to the conductance of disordered metals.

Analyzing magnetoresistance data, we find that the coherence time,  $\tau_\phi$ , shows a low temperature  $T$  dependence close to quasi-1D theoretical expectations ( $\tau_\phi \sim T^{-2/3}$ ) in 5 nm wide wires, while exhibiting a relative saturation as  $T \rightarrow 0$  for wide samples of the same material. Since an externally controlled parameter, the sample geometry, can cause a single material to exhibit both suppression and divergence of  $\tau_\phi$ , this finding provides a new constraint on models of dephasing phenomena.

**9:30 AM \*D10.4**

**NANOTECHNICS: DIRECT FABRICATION OF ALL-INORGANIC LOGIC ELEMENTS AND MICRO-ELECTRO-MECHANICAL SYSTEMS FROM NANOPARTICLE PRECURSORS.** Colin Bulthaupt, Eric Wilhelm, Brent Ridley, Joseph Jacobson, Massachusetts Institute of Technology, Media Lab, Cambridge, MA.

We have developed novel means for directly patterning of nanoparticle inks to form functional electronic structures and devices. In this paper we report on recent progress towards fabricating all-inorganic logic and micro-electro-mechanical systems (MEMS) using this approach.

**10:30 AM \*D10.5**

**SOLUTION DEPOSITED ORGANIC-INORGANIC HYBRID THIN FILM TRANSISTORS AND THEIR PATTERNING.** C.R. Kagan, D.B. Mitzi, C.D. Dimitrakopoulos, T.L. Breen, L.L. Kosbar, IBM T.J. Watson Research Center, Yorktown Heights, NY.

We report solution deposited organic-inorganic hybrid materials as the semiconducting channels in thin film field effect transistors. Organic-inorganic hybrid materials promise the high carrier mobilities of inorganic semiconductors and may be deposited as thin films by simple, low-cost, low-temperature solution-based techniques common for organic materials. Organic-inorganic perovskites, one subset of hybrid materials, self-assemble from solution to form oriented, molecular-scale composites of alternating inorganic perovskite sheets and organic layers. Spin-coated polycrystalline thin films of  $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{SnI}_4$ , just one example of an organic-inorganic perovskite, form semiconducting channels with field-effect mobilities of  $0.6 \text{ cm}^2/\text{V-sec}$  and on-off ratios of  $>10^6$ . The flexibility in the chemistry and dimensionality of the hybrids' components is exploited to prepare perovskites with alternate organic layers and inorganic frameworks, which is expected to improve carrier mobility and current modulation. We demonstrate an approach to pattern organic-inorganic hybrid thin films and electrically isolate many transistors on a substrate. Using microcontact printing we selectively coat substrates with self-assembled molecular monolayers to chemically differentiate their surfaces and upon solution deposition produce patterned thin films. This approach is more general to the patterning of solution deposited thin films and their precursors.

**11:00 AM D10.6**

**ASSEMBLING NANOWIRE ELECTRONICS AND OPTO-ELECTRONICS FROM NANOWIRE BUILDING BLOCKS.** Xiangfeng Duan, Yu Huang, Yi Cui, Charles M. Lieber, Harvard University, Dept of Chemistry and Chemical Biology, Cambridge, MA.

One dimensional structures represent the smallest dimension for efficient transport of electrons, holes and excitons, and thus can be used as building blocks for the assembly of nano-electronic and nano-optoelectronic devices. To achieve the potential of such structures will require readily available materials (nanowires) with variable and controllable electronic and optic properties. To this end, we describe a general synthetic approach - laser-assisted catalytic growth - to a wide range of semiconductor nanowires with controlled chemical composition and doping. Electrical characterization of individual GaAs and InP nanowires by two terminal, gate-dependent transport measurement demonstrate that these nanowires can be doped as either n- or p-type semiconductors in a controlled way. A rational approach for orthogonal assembly of nanowires into integrated multi-terminal devices such as crossed p-n junctions, light emitting diodes and tunneling diodes, will be presented. Electrical and opto-electrical characterization of these devices show clearly rectification and light emission. The implication of nanowire assembly for high density integrated nanoscale electronics and opto-electronics will be discussed.

**11:15 AM D10.7**

**TUNNELING MAGNETORESISTANCE OF SELF-ASSEMBLED COBALT-NANOCRYSTAL-SUPERLATTICE DEVICES.** C.T. Black, C.B. Murray, R.L. Sandstrom, S. Sun, IBM T.J. Watson Research Center, Yorktown Heights, NY.

We have combined chemical self-assembly with electron-beam lithography to produce sub-100 nm tunneling devices composed of ordered cobalt-nanocrystal arrays. In our devices the nanocrystal diameter is 10 nm, with interparticle spacings of  $\approx 2$  nm. These

magnetic superlattices are tunable model systems for studying magnetotransport in nanostructured materials, merging the nanometer size-scale of disordered granular thin films with the uniformity of larger-scale lithographically-defined arrays. Nanocrystal uniformity is reflected in device I-V characteristics, which are well-described by single-electron tunneling in an array of identical tunnel junctions. We measure a sharp voltage threshold for current onset, below which tunneling is exponentially-suppressed. Current above threshold scales with a power-law-dependence on applied voltage. We measure low-temperature magnetoresistance ratios of  $\sim 10$  percent, which approach the maximum predicted for spin-polarized tunneling in a randomly-oriented granular ferromagnetic film. Temperature- and bias-voltage dependence of the magnetoresistance indicate the presence of low-energy spin-flip scattering in the nanocrystal superlattice.

#### 11:30 AM D10.8

##### SYNTHESIS AND PROPERTIES OF MAGNETIC ARRAYS.

Sara A. Majetich, Dorothy Farrell, Carnegie Mellon University, Dept of Physics, Pittsburgh, PA.

Arrays of magnetic nanoparticles are a promising model system for studying magnetic interactions and have potential practical applications, particularly as data storage media. Forming magnetic arrays is difficult, however, because anisotropic magnetic dipole interactions favor chain formation over array growth. One approach to forming magnetic arrays is first to form a nonmagnetic array, and then to transform the material to a magnetic phase. Another approach is to coat magnetic particles with a nonmagnetic material, reducing the magnetic dipole interaction strength. We have pursued each of these methods. For the first system, we used monodisperse  $\beta$ -FeOOH nanorods, formed by dissolving iron (III) chloride in water. Settling by either gravity or centrifugation, these nanorods self assemble into stacked arrays called Schiller layers. The spacing between the layers is on the order of visible wavelengths, giving rise to iridescence by which the ordering can be recognized by naked eye observation. Schiller layers can be formed in particle dispersions with a concentration of  $5 \times 10^{14}$  particles/mL and a pH between 1.4 and 1.8. Once assembled, the system can be embedded in a solid matrix which will preserve the particle shape and uniformity, and therefore the ordering, while the transformation to the magnetic phase proceeds by annealing in a reducing atmosphere or electron beam irradiation. We have also coated small magnetic particle with silica. Monodisperse, spherical silica particles form close packed arrays; a composite magnetic particle/silica system is promising for magnetic array formation. The magnetic properties of the arrays are studied by SQUID magnetometry and compared with the behavior of isolated particles. Lorentz microscopy is used to characterize the magnetization direction of particles and the correlation between neighboring particles.

#### 11:45 AM D10.9

##### STRUCTURAL AND MAGNETIC PROPERTIES OF SELF ASSEMBLED Co AND CoFe NANOWIRES. H.R. Khan and K. Petrikowski, FEM, Materials Physics Department, Schwaebisch Gmuend, GERMANY.

Ordered nanowires have received considerable attention due to the interest in developing high density magnetic recording media (1,2). The magnetic properties such as coercivity ( $H_c$ ), ratio ( $M_r/M_s$ ) and magnetic energy product (B.H) depend on the composition, diameter, length and spacing of the nanowires. Cobalt nanowires of diameter in a wide range from 18 to 78 nm with spacing between 40 and 90 nm are electrodeposited into the self assembled pores of Al-1%Mg substrates obtained by anodic oxidation. Different electrolytes were used to obtain the various pore diameters. The anisotropic magnetic properties depend on the diameter and length of the nanowires as shown by the hysteresis loops. Maximum  $H_c$  and  $M_r/M_s$  values of 1850 Oe and 0.9 are observed for the Co nanowires of 18 nm diameter and 0.4  $\mu$ m length. The substitution of 10-20 wt% Fe for cobalt in the nanowires enhances the  $H_c$ ,  $M_r/M_s$  and the B.H values. And the enhanced values of  $H_c$  and  $M_r/M_s$  are 2275 Oe and 0.96 respectively. X-ray diffraction investigations show that Co nanowires consist of f.c.c. and h.c.p. phases whereas Fe-Co nanowires are of  $\gamma$ -phase. The layers of Co and Fe-Co are also electrodeposited on the Cu-substrates and their structural and magnetic properties are investigated and compared with the nanowires. The suitability of these nanowires for the high density recording media will be discussed.

1. H.R. Khan, O. Loebich and G. Rauscher, Thin Solid Films 275 (1996) 207-209.
2. H.R. Khan and K. Petrikowski, J. Magn. Magn. Mat. (In Press). This work is supported by Bundesministerium für Wirtschaft through Arbeitsgemeinschaft industrieller Forschungsvereinigungen e.V. and grant no (AIF 11429 N).

#### SESSION D11: 1D AND 3D SELF-ASSEMBLED SYSTEMS

Chair: John A. Rogers  
Friday Afternoon, December 1, 2000  
Constitution B (Sheraton)

#### 1:30 PM D11.1

##### SELF-ASSEMBLED GROWTH OF EPITAXIAL ERBIUM DISILICIDE NANOWIRES ON SILICON(001). Yong Chen, Douglas A.A. Ohlberg, Gilberto Medeiros-Ribeiro, Y. Austin Chang and R. Stanley Williams, Hewlett-Packard Laboratories, Palo Alto, CA.

By choosing a material that has an appropriate asymmetric lattice-mismatch to the host substrate, in this case  $\text{ErSi}_2$  on  $\text{Si}(001)$ , it is possible to grow one-dimensional epitaxial crystals.  $\text{ErSi}_2$  nanowires are less than one nanometer high, a few nanometers wide, close to a micron long, crystallographically aligned to  $\text{Si}\langle 110 \rangle$  directions, straight and atomically regular.

#### 1:45 PM D11.2

##### WIRING A MESOPOROUS INSULATOR WITH A NANOSCOPIC THREE-DIMENSIONAL WEB OF CRYSTALLINE RUTHENIUM DIOXIDE. Debra R. Rolison, Eric M. Lucas, Rhonda M. Stroud, Joseph V. Ryan, Alan D. Berry, Michele L. Anderson, Jeffrey W. Long, Veronica M. Cepak, Valerie M. Browning, and Celia I. Merzbacher, Naval Research Laboratory, Washington, DC.

We have developed a novel method to fabricate nanoscale electronic circuits in three dimensions by depositing nanoscale ruthenium dioxide on the interior surfaces of a mesoporous silica aerogel host. The  $\text{RuO}_2$  circuit, which overlays the silica network in a conformal fashion, is formed by cryogenic decomposition of ruthenium tetroxide onto the nanoscale silica network. Upon annealing the ruthenia-silica nanocomposite in oxygen to  $150^\circ\text{C}$ , interconnected, 4-nm diameter crystallites of  $\text{RuO}_2$  are formed without appreciable occlusion of the aerogel pore volume. Ruthenium dioxide nanowires offer a significant practical improvement in that, unlike metal or silicon nanowires,  $\text{RuO}_2$  can withstand both oxygen-rich and hydrous environments while maintaining high electronic conductivity. The host silica aerogel provides an insulating, low thermal conductivity, high surface area, highly porous architecture. The  $\text{RuO}_2$  self-wires a path over the  $400 \text{ m}^2 \text{ g}^{-1}$  of silica using only  $\sim 1\%$  of the silica surface and forms a web with numerous interconnected pathways. Wiring the interior of a mesoporous insulator permits direct electronic control and monitoring of chemical reactions in the pores. The  $\text{RuO}_2$ -wired silica aerogel serves, for example, as a porous catalytic electrode to electro-synthesize molecular chlorine from chloride. Other potential applications of such nanowired mesoporous architectures include use as a quantum-confined thermoelectric material, or as nanoscale electronic components for high-density circuits, especially in three dimensions. Ruthenium dioxide can now serve as a nanoscopic bottom electrode for more elaborate nanoelectronic circuits.

#### 2:00 PM \*D11.3

##### NANOSTRUCTURES AND NANOCOMPOSITES BASED ON POLYELECTROLYTE MULTILAYERS. M.F. Rubner, B. Chen, J. Choi, R.E. Cohen, P.T. Hammond, X. Jiang, T. Wang, Departments of MS&E and Chemical Engineering, MIT, Cambridge, MA.

Polyelectrolyte multilayers are ideal templates for creating thin film composites with spatially controlled domains of inorganic nanoparticles and micro-patterned surfaces. Using our understanding of pH controlled weak polyelectrolyte assembly, we have developed techniques to electrolessly plate various metals within and on top of multilayer films fabricated from poly(acrylic acid) and poly(allylamine hydrochloride). For example, by controlling the manner in which these two polymers are assembled and the number of free acid groups present at the surface, we have identified a means to either effectively promote the electroless plating of nickel metal or completely block the plating process. In addition, we have developed micro-contact printing techniques that make it possible to create polyelectrolyte multilayers with micron-scale patterned surfaces of electrolessly plated metals.

#### 2:30 PM \*D11.4

##### THREE-DIMENSIONAL ELECTRONIC SURFACES. J.C. Sturm, P.I. Hsu, M. Huang, H. Gleskova, S. Miller, A. Darhuber, S. Wagner, Z. Suo, and S. Troian, Center for Photonics and Optoelectronic Materials (POEM), Princeton University, Princeton, NJ.

The world of microelectronics is a flat one. Recently, however, there has been an interest in developing products with three-dimensional surfaces for applications such as electronic skins and perhaps someday even clothes and furniture. Over the past few years, several groups have groups have deformed devices and circuits on thin film substrates (such as plastic or stainless steel foils) to "developable" shapes, such as cylindrical surfaces or cones. In such cases the strain, which is what makes the deformation difficult, can be reduced by

simply reducing the substrate thickness. In this talk, we will discuss work towards the creation of microelectronics on spherical surfaces, in which case the strain encountered in deforming from a flat surface cannot be reduced by thinning the substrate. Both the deformation approach as well as that of direct fabrication on the spherical surface are being investigated. To plastically deform a flat sheet into a spherical cap shape results in a large strain which increases with the solid angle subtended. To create a cap covering a 66 degree field of view, an average strain of  $\sim 6\%$  will result, which will clearly crack inorganic device materials such as silicon. However, by creating "hard" device islands on "soft" substrates, large device islands are possible without cracks. To directly fabricate on a spherical surface requires pattern definition, for which both wet and dry micro-scaled printing techniques are being pursued. Tradeoffs of these methods vs. the deformation method for electronics on spherical surfaces will be presented.

### 3:30 PM \*D11.5

THE CONSTRUCTION OF POLYELECTROLYTE MULTILAYERS IN THREE DIMENSIONS. Xueping Jiang, Sarah L. Clark, Shoshana Gourdin, and Paula T. Hammond.

Our group has demonstrated that we can manipulate interactions between polyions and surfaces to create patterned polyelectrolyte multilayer films. Secondary as well as electrostatic interactions can be used to drive deposition on specific regions of a surface, creating lateral arrays of polyelectrolyte multilayers consisting of two or more components. We are also able to create 3-dimensional structures, including patterns atop patterns, utilizing a new approach to functionalizing polyelectrolyte multilayer surfaces with graft and block copolymers. This approach has allowed us to put down multiple level patterns on surfaces. This talk will address each of these approaches to building dimensional thin films, and the role and importance of surface-polymer interactions in each case.

Measurements of the surface interactions that are critical to these approaches are currently underway using chemical force microscopy. Examples and possible applications will also be addressed.

### 4:00 PM \*D11.6

NANO- TO MICROSCALE PATTERNING OF POLYMERS USING SELF-ASSEMBLY AND EXTERNAL FIELDS. Thomas P. Russell, Thomas Thurn-Albrecht, Jason DeRouchey, Zhiqun Lin, Tobias Kerle, Polymer Science and Engineering Dept, University of Massachusetts, Amherst, MA; Erik Schaeffer, Ullrich Steiner, Department of Chemistry, University of Groningen, THE NETHERLANDS.

Patterning thin films of polymers requires control over the surface and interfacial energies of the polymers and any inherent morphologies. Control can be achieved with external fields, e.g. electric fields where high field strengths can be achieved with low voltages; with controlled interfacial interactions by chemical modification of solid surfaces; or by use of commensurability conditions where natural length scales of the polymer morphology can be balanced constrained by the film thickness. With such control simple, robust routes are accessible for the generation of well-defined, well-ordered structures over large areas from anoscopic to macroscopic length scales. These structures can be subsequently used in standard, lithographic processes to produce materials with novel magnetic and electric properties.

### 4:30 PM D11.7

BASIC: BIO-INSPIRED ASSEMBLY OF SEMICONDUCTOR INTEGRATED CIRCUITS. R. Bashir, S. Lee, X. Zu<sup>a</sup>, D. Bergstrom<sup>a</sup>, H.A. McNally, D. Janes School of Electrical and Computer Engineering, <sup>a</sup>Dept. of Medicinal Chemistry, Purdue University, W. Lafayette, IN.

In recent years, biologically-inspired self-assembly of artificial structures, some with useful optical properties, has been demonstrated. However, to date there has been no demonstration of self-assembly of useful electronic devices for the construction of complex systems. In this project, new approaches towards the development of future hybrid bio-electronic devices and systems are being explored. The main theme is to use the mutual binding (hybridization) and specificity of DNA strands (oligonucleotides) for the assembly of useful silicon devices. Novel silicon-on-insulator (SOI) processing techniques are being used to make devices which can be 'released' from their host substrate into a liquid medium. These devices are  $4\mu\text{m} \times 4\mu\text{m} \times 2.5\mu\text{m}$  in size (to be scaled down to nano-meters in the future) and have gold on one surface. Thiol-derivatized single stranded DNA molecules can be attached to these gold surfaces on the devices. Meanwhile, a substrate will be prepared with 2-D gold interconnect layers, which will also be functionalized with short single stranded oligonucleotides. The free-floating active devices will be released onto the patterned/functionalized substrate, in a liquid medium, along with oligonucleotides that will bind to and connect the DNA strands on the substrate and on the device. Consequently, these silicon devices will use thermal energy to

self-assemble onto the interconnect layers, according to the hybridization patterns of the complementary strands of DNA. Other molecules such as xylyl dithiol are also being investigated as the means for the attachment of the Au-coated silicon devices selectively to the substrate. This approach can be used to assemble nano-scale devices and circuits and can also be a powerful technique for heterogeneous integration of materials (e.g. Si on Glass or polymer). Preliminary results regarding the fabrication and release of the device islands will be presented.

### 4:45 PM D11.8

SELF-ASSEMBLED MONOLAYER STACKS OF ORIENTED LYOTROPIC CHROMONIC LIQUID CRYSTALS. Tod Schneider, Oleg Lavrentovich, Chemical Physics Interdisciplinary Program, Liquid Crystal Institute, Kent State University, Kent, OH.

A simple method to create in-plane oriented monolayer stacks using a lyotropic chromonic liquid crystal (LCLC) dye is presented. The method is based on alternate layer-by-layer adsorption of polyions and dyes from aqueous solutions. As the dye we use is in the liquid crystalline phase, it may be shear-oriented during deposition. This orientation is preserved during adsorption onto the substrate surface. Hence, one may stack alternate monolayers of dye and polyion while controlling the in-plane orientation of the dye within the layers. Controlling the absorption axis of the dye allows one to create thin (3-100 nm) films with unique optical properties; e.g., a thin visible light polarizer is presented. This technique could be easily adapted to create polarizers, alignment layers, filters, optical retarders or compensators. Furthermore, this technique provides a new method for producing inexpensive integrated optical components; e.g., plastic substrates for liquid crystal displays containing polarizing-compensating-filtering-alignment layers manufactured on one continuous (roll-to-roll) fabrication line.